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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

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THE

CHEMICAL GAZETTE.

No. CXXV.—January 1, 1848.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Further Researches on the Fluids of the Flesh. *By* Prof. Liebig.

In two former numbers* we gave a brief account of the important and interesting discovery by Prof. Liebig of the general presence of kreatine and some new substances in the fluids of the flesh of animal bodies. We shall now enter somewhat more fully upon their consideration.

We have already mentioned, that by the action of strong mineral acids upon kreatine a new substance is produced; this is a true organic alkali, and is called kreatinine. The action of mineral acids upon kreatine is very remarkable. A solution of kreatine, to which, while cold, hydrochloric acid is added, yields on spontaneous evaporation crystals of unchanged kreatine; but when heated with strong hydrochloric acid, a solution of kreatine no longer yields crystals of that substance. The same result is obtained with sulphuric, phosphoric and nitric acids. When dissolved in one of these acids and the solution gently evaporated, crystals are obtained, which are very soluble in alcohol, a property not belonging to kreatine. These crystals contain a portion of the acid employed, in a state of combination; during the action the new body kreatinine is formed. Kreatinine is crystalline, the crystals belonging to the monoklinometric systems. It is soluble in 11·5 parts of water at 60° F., and much more so in hot water. The aqueous solution restores the blue colour of reddened litmus, and a crystal laid upon moist turmeric-paper causes a brown stain. It is soluble in boiling alcohol, and recrystallizes on cooling. At 60° F. 1000 parts of alcohol dissolve 9·8 parts of kreatinine.

In its chemical characters it is exactly analogous to ammonia.

When it is added to a moderately-strong solution of nitrate of silver, a mass of small white needles is instantly formed; these are very soluble in hot water, and crystallize from it unchanged on cooling. They consist of a basic compound of kreatinine and nitrate

* Chem. Gaz., vol. v. pp. 67 and 81.

of silver. Kreatinine immediately causes a white curdy precipitate in a solution of bichloride of mercury, which in a few minutes changes to a mass of slender transparent colourless needles.

In a neutral aqueous solution of chloride of zinc, kreatinine instantly causes a granular crystalline precipitate, appearing under the microscope formed of very small needles concentrically grouped.

Kreatinine expels ammonia from ammoniacal salts, and forms crystallizable double salts of a fine blue colour with salts of copper.

When dilute solution of hydrochlorate of kreatinine is mixed with bichloride of platinum, no precipitate is produced; but on evaporation at a gentle heat, deep yellow transparent crystals are formed, which are very soluble in water, but less so in alcohol. They are composed of a double salt, analogous to the double chloride of platinum and ammonium.

Crystallized kreatinine, heated to dryness at 212°, loses 12·08 per cent. of water. When exposed to a current of hydrochloric acid gas, it increases but little in weight; water is given off and hydrochloric acid absorbed, the latter amounting to 24·68 per cent.

The conversion of kreatine into kreatinine by the mineral acids depends upon the separation of 4 equivs. of water. Kreatine is composed as follows:—

	Found.			
Carbon	42·54	8	48 =	42·48
Hydrogen	6·38	7	7	6·19
Nitrogen	37·20	3	42	37·17
Oxygen	13·88	2	16	14·16
			113	

Hence kreatinine contains the elements of 1 atom of caffeine + 1 atom of amide, $C^8 H^5 N^2 O^2 + NH^2 = C^8 H^7 N^3 O^2$.

On comparing the results of the analyses of kreatine and kreatinine with the composition of the substance discovered by Pettenkofer in human urine, we perceive at once that both kreatine and kreatinine must stand in a certain relation to that body. The substance from urine contains 1 equiv. of water less than anhydrous kreatine, and 1 equiv. more than kreatinine.

Pettenkofer's substance may be obtained from urine by a more simple process than the one proposed by him. It is this:—Neutralize the urine with milk of lime, and then add solution of chloride of calcium as long as it causes a precipitate of phosphate of lime. Filter the liquid, and evaporate until the salts crystallize on cooling. The mother-liquor is separated from the salts without the use of alcohol, and mixed with a syrupy solution of neutral chloride of zinc, in the proportion of about ½ an oz. to 1 lb. of the extract. In three or four days the greater part of Pettenkofer's zinc compound is found to have crystallized in rounded yellow grains. The deposit is well-washed in cold water, then dissolved in boiling water, and hydrated oxide of lead added to the solution until it acquires a strongly-alkaline reaction. By this means the zinc and hydrochloric acid are separated in an insoluble form, while the substance formerly

combined with them remains in solution. This is now decolorized with blood-charcoal, which also removes a trace of oxide of lead, and the filtered liquid is evaporated to dryness.

By this, as also by Pettenkofer's process, a white crystalline substance is obtained, having the same characters in each case. But this is a mixture of kreatinine with kreatine, which may be separated by hot alcohol, in which the former is easily soluble, the latter very sparingly so. On analysis these two substances yielded—

	Kreatine from urine (anhydrous).	Kreatinine from urine.
Carbon	36·90	42·64
Hydrogen	7·07	6·23
Nitrogen	32·61	37·41
Oxygen	23·42	13·72
	100·00	100·00

If we compare these numbers with those obtained on the analysis of kreatine from flesh and of kreatinine prepared from it, it is obvious that they are respectively identical.

In urine which had become putrid, kreatinine alone was found, without a trace of kreatine.

The kreatine in Pettenkofer's zinc-compound is an accidental and variable ingredient; for a warm solution of kreatine is not precipitated by chloride of zinc, and the crystals which are deposited contain neither zinc nor chlorine, but possess all the characters of pure kreatine. Its formation is as follows:—If fresh urine contain kreatinine in combination with an acid and free kreatine, when it is neutralized by an alkali, the kreatinine will be set free; and when the liquid is concentrated to one-twentieth of its original volume, the addition of chloride of zinc will precipitate the compound of chloride of zinc with kreatinine; but the crystals of this substance will be mixed with those of kreatine whenever the quantity of the latter present is more than the liquid can retain in solution when cold.

Hydrochlorate of Kreatinine.—This salt is readily soluble in boiling alcohol, and crystallizes from it in short, transparent, colourless prisms, very soluble in water; on evaporating its aqueous solution, it is obtained in broad transparent scales, having an acid reaction. It yielded on analysis—

	Found.			
Carbon	32·48	8	48 =	32·30
Hydrogen	5·30	8	8	5·35
Nitrogen	28·27	3	42	28·11
Oxygen	10·54	2	16	10·55
Chlorine	23·41	1	35·4	23·69
			149·4	100·00

Platinum-salt.—This is obtained by adding solutions of bichloride of platinum to hydrochlorate of kreatinine and gentle evaporation, when it separates in red prisms; when more rapidly formed, in yellowish-red transparent grains. It consists of—

	From flesh.	From urine.	Calculated.
Kreatinine and hydrochloric acid..	69·47	69·05	69·05
Platinum	30·53	30·95	30·95
	100·00	100·00	100·00

Sulphate of Kreatinine is obtained by adding dilute sulphuric acid to a boiling saturated solution of kreatinine until a strongly acid reaction appears, and evaporation; it forms a white saline mass, soluble in hot alcohol. The solution on cooling becomes milky, and deposits transparent, concentrically-grouped, four-sided tables of neutral sulphate of kreatinine, which remain transparent at 212° F., and consist of—

				Calculated.
Sulphuric acid		1	24·65	24·69
Kreatinine ..	Carbon	8	29·33	29·63
	Hydrogen	8	5·03	4·94
Water	Nitrogen.....	3	25·44	25·92
	Oxygen	3	15·55	14·82
			100·00	100·00

Sarcosine.—This substance is obtained by boiling a saturated solution of kreatine with crystallized hydrate of baryta, 10 parts of the latter being used for each part of the kreatine in the solution. Ammonia is evolved, and the fluid becomes turbid, and deposits a white crystalline powder, the formation of which continues as long as the evolution of the ammonia lasts. When, after the addition of hydrate of baryta and water from time to time and continued boiling, ammonia ceases to be evolved, we obtain on filtration a clear colourless liquid, which contains the new substance and caustic baryta, carbonate of baryta remaining on the filter. On separating the excess of baryta by a current of carbonic acid and boiling, the baryta is separated from the organic base which remains in the solution; and on evaporation, the latter yields a syrup, which when set aside solidifies to a mass of broad, colourless, transparent laminæ. In the preparation of the sarcosine pure baryta must be used; and the latter must be previously tested for potash, lime, chlorine and nitric acid, and separated from them, as all these impurities are with great difficulty separated from the new base.

To prepare pure sarcosine, it must be converted into sulphate, and the pure base obtained from this salt. For this purpose dilute sulphuric acid is added to the residue of the evaporation of the filtrate until a strongly acid reaction is produced, the mixture evaporated in a water-bath, alcohol added to the syrupy residue, and the whole stirred with a glass rod. The syrupy sulphate then solidifies, forming a white crystalline powder, which is washed with alcohol in the cold, then dissolved in water and heated with pure carbonate of baryta until effervescence ceases and the acid reaction of the fluid has disappeared. It is then filtered, evaporated to a syrup in a water-bath and set aside, when in from twenty-four to thirty-six hours it crystallizes in colourless right-rhombic prisms; these are very soluble in water, but difficultly in alcohol, and insoluble in

æther. On drying at 212° F. they retain their aspect; at a somewhat higher temperature they fuse, and are volatilized without residue. When exposed for a considerable time between two watch-glasses to a temperature of 212°, the upper glass becomes lined with a net-work of crystals of sublimed sarcosine. On analysis sarcosine yielded—

	Found.			Calculated.
Carbon	40·73	40·90	6	40·45
Hydrogen	7·90	7·82	7	7·86
Nitrogen	15·84	15·90	1	15·73
Oxygen	35·53	35·38	4	35·96

The aqueous solution of sarcosine exerts no action upon vegetable colours. It possesses a sweetish, sharp, somewhat metallic taste, and produces no precipitate in dilute solutions of nitrate of silver and bichloride of mercury. If, however, a crystal of sarcosine be placed in a cold saturated solution of bichloride of mercury, it is immediately dissolved, and in a short time a number of fine, transparent needles of a double salt are formed. When sarcosine is added to a solution of acetate of copper, the latter assumes a deep blue colour, as with ammonia; and on gentle evaporation a double salt of the same colour is formed.

When evaporated with muriatic acid, a white saline mass is obtained, which crystallizes from hot alcohol in small transparent grains and needles.

Excess of bichloride of platinum does not produce any precipitate in a solution of muriate of sarcosine. If, however, the mixture be allowed to evaporate spontaneously, broad flattened octohedra, of a honey-yellow colour, are speedily produced. When the excess of chloride of platinum is removed by a mixture of alcohol and æther, the crystals are obtained in a state of purity. This salt, when dried in the air, loses 6·7 per cent. of water at 212° F. It yielded on analysis—

	Found.		Calculated.
Sarcosine Muriatic acid Chlorine	66·40	1 1 2	66·55
Platinum	33·60	1	33·45
	100·00		100·00

The crystallized double salt contains 2 atoms = 5·7 per cent. of water.

Sulphate of Sarcosine.—Its preparation has been already described (p. 4). When the residue washed with cold alcohol is boiled with 10 or 12 parts of alcohol, it dissolves, leaving traces of sulphate of baryta; and on cooling, the solution deposits transparent, colourless, four-sided tables of great lustre, closely resembling chlorate of potash in appearance; they are difficultly soluble in cold alcohol, but very readily in water, and crystallize from the latter solution in large feathery plates. Both the aqueous and the alcoholic solution of this acid react strongly acid, so that it cannot be determined

when the washing is completed. Hence the following analyses of this salt have yielded too much sulphuric acid :—

	Dried at 212°.		Calculated.	
Sulphuric acid	29·25	30·36	28·98	1
Water	70·75	69·64	71·02	1
Sarcosine				1
	100·00	100·00	100·00	

The formula $C^6 H^7 NO^4 + HO$ would give in 100 parts—

	Analysis.				Theory.
Carbon	36·34	35·69	36·28	6	36·73
Hydrogen	7·90	8·16	8·25	8	8·16
Nitrogen	..	..	..	1	
Oxygen	..	..	..	5	

The formation of sarcosine from kreatine may be thus explained:— If we deduct the elements of the former from those of crystallized kreatine, the remaining formula corresponds accurately to that of urea :—

1 equiv. kreatine	$C^8 H^{11} N^3 O^6$
1 equiv. sarcosine	$C^6 H^7 N O^4$
	$C^2 H^4 N^2 O^2$

It is thus evident, that on decomposing kreatine by baryta, carbonic acid and ammonia are secondary products of the decomposition of urea. I detected urea in the liquid before the completion of the decomposition of the kreatine.

According to the above formula of sarcosine, it contains the same elements in the same relative proportion as lactamide which Pelouze discovered, and urethane discovered by Dumas; but its insolubility in æther and alcohol sufficiently distinguishes it from these two substances.

Sarcosine and urea are not the only products of the decomposition of kreatine by baryta; for when water is added to the alcohol from which the sulphate of sarcosine has crystallized, the fluid neutralized with carbonate of baryta, and the neutral solution evaporated to a thin syrupy consistence, long before reaching the point at which the sarcosine would have crystallized, long colourless prisms are deposited, which exert a very feeble acid reaction, and which I at first thought to be an acid; but they fuse and volatilize without leaving any residue of baryta. They are readily soluble in water and alcohol, also in about 30 parts of æther; the aqueous solution is not precipitated by acetate of lead, lime- or barytic salts. This substance has not been further examined.

Inosinic Acid.—When the mother-ley of the juice of flesh, after all the kreatine has crystallized out, is further evaporated, and small portions of alcohol are gradually added until it becomes milky; if set aside for several days, yellow or white, granular, leafy or needle-shaped crystals are deposited, which may be separated by filtration from the inspissated mother-ley and washed with alcohol.

These crystals consist of a mixture of several substances, among which kreatine is always present. The principal constituent, however, is a potash- or baryta-salt of a new acid, which I shall designate *Inosinic Acid.*

If the whole of the phosphoric acid was not precipitated by baryta, the crystals contain inosinate of potash; if the baryta was in excess, they consist of inosinate of baryta or a mixture of both salts. To separate the acid, the deposit is dissolved in hot water, and chloride of barium added to the solution; on cooling, crystals of inosinate of baryta are then obtained, which after a second crystallization are perfectly pure. The acid is readily obtained pure from the barytic or copper-salt; from the former by the precipitation of the baryta with dilute sulphuric acid, from the latter by decomposition with sulphuretted hydrogen. The solution obtained by the decomposition of the copper-salt is usually turbid and brown from the suspension of sulphuret of copper, but it is rendered colourless by a little blood-charcoal.

The dilute inosinic acid obtained in each case reacts strongly acid, and possesses an agreeable taste of broth; on evaporation it leaves a syrup, which does not crystallize even when set aside for a week; when treated with alcohol, the thick liquid is converted into a pulverulent, solid, hard mass, traces of which only are soluble in alcohol; the acid is precipitated from a concentrated aqueous solution by alcohol in white uncrystalline flakes; it is insoluble in æther. I had not enough of the acid for analysis. The barytic salt on analysis yielded—

				Calculated.
Carbon	24·46	24·80	10	23·96
Hydrogen	2·64	2·59	6	2·40
Nitrogen	11·37	11·37	2	11·18
Oxygen	31·46	30·79	10	31·95
Baryta	30·51	30·07	1	30·51
	100·00	100·00		100·00

On deducting the baryta, the anhydrous acid contains 10 equivs. of carbon, 6 atoms of hydrogen, 2 nitrogen, and 10 oxygen. If the baryta in this salt be admitted to occupy the place of an atom of water, the formula of inosinic acid is $C^{10} H^{7} N^{2} O^{11}$.

Inosinates.—Free inosinic acid causes no precipitate in lime- or baryta-water; but on repose and spontaneous evaporation, transparent pearly plates of inosinate of baryta and lime form in these mixtures. The free acid, as also its soluble salts, precipitate acetate of copper, producing a beautiful greenish-blue precipitate, which is insoluble in boiling water and is not blackened by ebullition. Inosinates yield a white precipitate with salts of silver; the precipitate is gelatinous, resembling hydrate of alumina in aspect, and is soluble in nitric acid and ammonia. Inosinic acid produces a white precipitate in salts of lead. The alkaline salts of this acid are decomposed when heated on platinum-foil, diffusing a strong and agreeable odour of roast meat.

Inosinate of Potash is obtained from the barytic salt by the careful precipitation of the baryta with carbonate of potash, as also directly from the juice of flesh (p. 7). It is very soluble in water, and crystallizes from it in delicate, long, four-sided prisms. It is insoluble in alcohol, and is precipitated from it, even from dilute solutions, in the form of a granular powder. On adding alcohol to a moderately-concentrated solution of the potash-salt, the latter solidifies to a mass of delicate pearly plates. The potash-salt obtained immediately from the juice of the flesh was dissolved in water and precipitated with nitrate of silver, the precipitate washed, and the potash determined from the filtrate as nitrate. When dried at 212° F., the salt lost 22·02 per cent. of water of crystallization.

Inosinate of Soda crystallizes in delicate silky needles. It is extremely soluble in water, but insoluble in alcohol.

Inosinate of Baryta.—This salt is very difficultly soluble in cold water, more readily in hot, and insoluble in alcohol. 1000 parts of water at 61° F. dissolve 2·5. Its solution in hot water exhibits the same peculiarity as that of the phosphovinate of baryta. When an aqueous solution, saturated at about 158° F., is heated to ebullition, a portion of the salt is precipitated in the form of a resinous mass; and whilst water at from 140°–158° F. dissolves a portion of the salt, on treating it with the same quantity of boiling water part always remains undissolved; and this residue, on longer ebullition with water, undergoes a change, whereby it loses its solubility in water of a lower temperature also.

The crystals of the barytic salt form elongated, four-sided, pearly plates; when dried they resemble polished silver; at 212° F. the crystals lose water, becoming dull and opake; they soon effloresce in dry air. They lose 19·07 per cent. of water when dried at 212°. If the barytic salt contained 7 atoms of water, like the potash-salt, they would have lost 20 per cent.

Inosinate of Copper.—When dried this salt forms a light blue uncrystalline powder; it is almost entirely insoluble in water, ferrocyanide of potassium only producing such a reddening as it would in copper-salts diluted to $\frac{1}{50000}$th; it is insoluble in acetic acid, readily soluble in ammonia with a blue colour.

Inosinate of Silver.—The gelatinous precipitate produced in silver-salts by soluble inosinates is somewhat soluble in pure water, less so in water containing nitrate of silver in solution; it is little, if at all, blackened by light.

The precipitate obtained in the analysis of the potash-salt was decomposed with sulphuretted hydrogen, and the sulphuret of silver thus obtained converted into chloride of silver. The dried potash-salt yielded by this method 49·99 per cent. oxide of silver. If the composition of the silver-salt was analogous to that of the potash-salt, it would have yielded 51·02 per cent. oxide of silver. This difference is considerable; but such errors are unavoidable in performing so many operations on one and the same quantity of substance.

Inosinic acid appears from its composition to belong to the binary

acids; considered as a hydrate, it contains the elements of anhydrous acetic acid, oxalic acid and urea:—

Acetic acid	$C^4 H^3 O^3$
Oxalic acid	$C^4 O^6$
Urea	$C^2 N^2 H^4 O^2$
Hydrated inosinic acid	$C^{10} N^2 H^7 O^{11}$

When the acid is heated with peroxide of lead, with the addition of dilute sulphuric acid, the peroxide becomes white; the filtered solution, freed from the excess of sulphuric acid, deposits on evaporation needle-shaped crystals; when mixed in the concentrated state with nitric acid, no precipitate is produced; but on evaporation, small, colourless, granular crystals are obtained, which were not further examined.

The temperature at which the juice of flesh is evaporated exerts great influence in obtaining the inosinates. In several instances, when the temperature has never exceeded 212° F., I have obtained no traces of inosinate of potash or baryta; whilst the juice of the flesh of the same animal yielded considerable quantities when during the evaporation a strong current of air was conducted over the surface of the liquid, and thus its temperature was retained at about 122° or 140° F.—Liebig's *Annalen* lxii. p. 257.

On the Behaviour of the Perchloride of Iridium towards Nitrate of Silver. *By* C. Claus.

It is well known that nitrate of silver does not precipitate as usual chloride of silver from the solutions of the chlorides of the metals accompanying platinum, but a combination of it with the chlorides of these metals. The reaction of nitrate of silver upon the potassio-chloride of iridium is highly remarkable, and has been previously recommended by the author as the best method of ascertaining the presence of iridium. At the commencement of the action, a dark indigo-blue flocculent precipitate is obtained, which soon loses its colour; the precipitate contains silver, chlorine, and the whole of the iridium; the supernatant liquid is colourless, and contains free nitric acid, nitrate of potash, and the excess of nitrate of silver. The precipitate has the composition $3AgCl + Ir^2Cl^3$; the perchloride of iridium has consequently passed into the sesquichloride, and the salt has the formula of the other double compounds of the sesquichloride. From $3(AgO, NO^5) + 2(KCl, IrCl^2)$ there must be formed in this reaction $3AgCl + Ir^2Cl^3 + 2(KO, NO^5) + NO^5 + O$; consequently oxygen must be eliminated. The author suspects that the blue colour at the commencement of the reaction is owing to the precipitation of the hydrated oxide of iridium, which subsequently passes into the sesquioxide with loss of oxygen, and now decomposes a portion of the chloride of silver. It is extremely probable that the whole of the silver is at first precipitated as chloride of silver, while the metals, potassium and iridium, are converted into oxides, the latter of which does not combine with nitric acid, and

so falls along with the chloride of silver. If we admit this explanation, the property of the hydrated oxide of iridium, of uniting with the chloride of silver, must be ascribed to it in its nascent state, as hydrated oxide of iridium mixed with free nitric acid and chloride of silver is not converted into that compound. The sesquichloride of silver and iridium is insoluble in water and acids, and very sparingly soluble in ammonia. When a strong solution of ammonia is poured over it, it is converted in the course of a few days into microscopic rhomboidal crystals, of a diamond lustre and a light yellow colour with a greenish tint, which possess the same composition. In analysing this substance, it was mixed with carbonate of soda and gently heated to redness. The chloride of sodium formed was extracted with water, and the chlorine in the solution estimated in the usual manner. The silver was removed from the residue of metal by dilute nitric acid, which however dissolved some of the iridium, so that the determination of the silver generally came out too high. The results of the analyses are—

Chlorine.....	27·82	28·03	29·10	6	=2655·84	28·96
Silver.....	46·36	45·01	44·00	3	4054·80	44·15
Iridium	25·32	26·96	26·90	2	2467·00	26·89

On the Action of Sulphuretted Hydrogen upon Nitric Acetene. *By* T. S. Hunt.

In my communication of May 29*, on the relations between glycocoll and alcargene, I stated that nitric acetene (the hyponitrite of oxide of ethyle of Liebig) is decomposed by sulphuretted hydrogen with the separation of sulphur; and suggested that from analogy we might expect the formation of a new alkaloid, which, from the known tendency in bodies of the acetic series to polymorphosis†, might be derived from the elements of 2 equivs. of the æther, and possess the composition $C^8 H^{12} N^2 O^2$, having the same relation to glycocoll that alcarsine has to alcargene. Although my subsequent experiments have not verified this conjecture, they have led to the discovery of a new reaction, which is not without interest.

* See Chem. Gaz., vol. v. p. 386.

† M. Gerhardt has proposed to designate by the following terms the four kinds of metamorphosis which embrace all the chemical transformations of organic bodies:—1. *Symmorphosis*; this includes those reactions which consist in the direct addition or fixation of another substance, as the combination of the alkaloids with acids and of chlorine with certain hydrocarbons. 2. *Apomorphosis*; this denotes such changes as are produced by the subtraction or elimination of certain elements; thus salts of ammonia lose the elements of water and become amids, and acids in the same manner yield anhydrids. 3. *Polymorphosis*; this represents a multiplication or combination of two or more equivalents of a compound. Thus three atoms of aldehyde unite to produce a new isomeric body, and under the influence of ammonia three equivalents of benzoilol coalesce to form with it one of hydrobenzamid. 4. *Diamorphosis*; this implies a division or breaking up of a compound into simpler forms, as when an equivalent of cyanuric acid is resolved by heat into three of cyanic acid; or glucose, under the influence of certain ferments, into carbonic acid gas and alcohol.

The æther employed in the following experiment was prepared after Liebig's method, by passing the nitrous vapours, evolved by the action of nitric acid upon starch, into a carefully cooled mixture of alcohol and water, and condensing the volatile product in a tube surrounded by ice. It was washed two or three times with water, and finally dried by chloride of calcium. Thus prepared, it had all the characters assigned by Liebig to the pure æther.

I. An alcoholic solution of the æther, mixed with a little water of ammonia, was placed in a tubulated retort surrounded by ice and connected with a condensing apparatus. A slow current of sulphuretted hydrogen was now passed through the liquid, which assumed a dark orange colour, and almost immediately began to deposit sulphur. Considerable heat was evolved, and a portion of the æther distilled over unchanged. When the separation of the sulphur had ceased, and the deep yellow fluid gave evidence of the presence of hydrosulphuret of ammonia, a solution of the æther was added in small portions until the mixture no longer discoloured the salts of lead. It was now carefully neutralized by dilute sulphuric acid, and distilled in a water-bath to one-half. The residue in the retort was carefully examined, and was found to be simply sulphate of ammonia. The alcoholic distillate had a slightly alliaceous odour like mercaptan. In one experiment, operating upon æther, probably impure, a liquid was obtained with a powerful taste and odour recalling that of garlic.

II. About 50 grs. of the æther were introduced into a glass globe, and a stream of pure moist sulphuretted hydrogen was conducted to the bottom. The globe was immediately filled with a white cloud, and the sides were soon coated with pure sulphur, which was precipitated in such abundance as to make the liquid at the bottom quite thick. When the reaction was finished, the contents of the globe were washed out with a little water; the liquid was alkaline to turmeric paper. A little hydrochloric acid was added, the liquid boiled, filtered, mixed with a solution of chloride of platinum, and evaporated to dryness in a water-bath. The residue, washed with alcohol, left a quantity of yellow salt, which under a magnifier presented the form of brilliant octahedrons, which were readily recognised as the ammoniochloride of platinum.

III. These experiments led to the conclusion, that the reaction resulted in the complete decomposition of the nitric acetene into ammonia and alcohol, and the following experiments placed this beyond a doubt. Having ascertained that the alkaline sulphurets and hydrosulphurets effected this decomposition, a solution of 20 grs. of hydrate of soda was saturated with sulphuretted hydrogen. This was mixed with about 2 oz. of dilute alcohol and 300 grs. of the æther, and the solution being carefully cooled by ice, a slow current of sulphuretted hydrogen was passed through until the decomposition was completed. An alcoholic solution of the æther was then carefully added to decompose the excess of the gas in the solution; it was then separated from the precipitated sulphur, and neutralized by dilute sulphuric acid. The liquid gave an abundant yellow crystalline precipitate with chloride of platinum, and contained a large

quantity of sulphate of ammonia, besides which nothing but the salt of soda could be detected.

IV. *A dilute solution* of hydrosulphuret of ammonia was placed in a strong bottle with a well-ground stopper, and cooled by a bath of ice and water. A small portion of the æther was then added, and the bottle immediately closed. The reaction was violent, and owing to the great volatility of the æther it was necessary to confine the stopper; when the action was finished another portion was introduced, until by successive additions of hydrosulphuret of ammonia 250 grs. were decomposed. The clear liquid was then separated from the precipitated sulphur, neutralized by dilute sulphuric acid, and agitated with oxide of lead to remove the excess of sulphuretted hydrogen; it was then submitted to distillation in a water-bath until about 200 grs. of liquid had passed over. This had the smell and taste of dilute spirit of wine; when warmed with a mixture of bichromate of potash and sulphuric acid, the latter was readily reduced with the evolution of aldehyde, which was at once recognised by its odour.

In this reaction 1 equiv. of nitric acetene and 6 of sulphuretted hydrogen yield 1 of alcohol, 1 of ammonia, 2 of water, and 6 of sulphur:—

$$C^4 H^5 NO^4 + 6HS = C^4 H^6 O^2 + NH^3 + 2HO + 6S.$$

As M. Laurent has lately confirmed the observations of M. Gerhardt, that nitric acetene is produced by the action of nitric acid upon brucine, we are enabled by this reaction to form alcohol by a new process, independent of the fermentation of glucose, and from a compound much higher in the organic scale.

The nitric æther of wood-spirit, *nitromethol*, is also decomposed by hydrosulphuret of ammonia, although less rapidly than the nitric acetene; crystals of sulphur separate, and the liquid contains a volatile compound of a powerfully alliaceous odour, resembling that of mercaptan. I have not been able to examine it further.

P.S. Since the above was written I have received the 'Journal de Pharmacie et de Chimie,' from which I learn that M. Emile Kopp has already investigated the action of sulphuretted hydrogen upon nitric acetene*, and has arrived at the same result as myself. But as the remarks in my last communication (vol. v. p. 386) require some explanation, I here publish my results and an account of the processes employed. M. Kopp has also shown that the nitric æther (nitrate of oxide of ethyle of Liebig) is decomposed in a similar manner by hydrosulphuret of ammonia with the production of ammonia and sulphur-alcohol or mercaptan.—Silliman's *Journal*, Nov. 1847.

On the Action of Bases on Pentathionic Acid. *By* H. Ludwig.

A saturated solution of sulphurous acid was treated with sulphuretted hydrogen until it retained the odour of the latter gas. The solution of sulphuretted pentathionic acid thus formed was divided into two equal portions, and the one half saturated with carbonate

* See this Journal, vol. v. p. 237.—Ed. *Chem. Gaz.*

of potash. The sulphur which separated was removed by filtration, and the liquid mixed with the other half of the pentathionic acid. A further deposit of sulphur resulted, which was filtered. The clear liquid possessed an acid bitter taste, strongly reddened blue litmus-paper, and might be heated to boiling without losing its property of precipitating the protonitrate of mercury. On evaporating it, a gas escaped with the aqueous vapour, which strongly irritated the eyes; and from the clear liquid, after some time a colourless salt separated in transparent rhombic prisms, pointed at the four terminal surfaces. A second evaporation of the mother-ley yielded the same crystals. On a third evaporation, sulphur separated from the acid liquid. This salt contains less sulphur than the pentathionate of potash. It is a double salt of the pentathionate and tetrathionate of potash, $KOS^5O^5 + KOS^4O^5$ or $2KOS^9O^{10}$. The solution of this compound has nearly the same properties as the pentathionic acid and its salts, but it may be distinguished from the latter by its behaviour towards strong alcohol; tetra-pentathionate of potash separates on the addition of this agent in a crystalline state, while pentathionate of potash remains in solution. The solution of the tetra-pentathionate may be retained at a boiling temperature for a considerable length of time without the salt being decomposed; but if a certain quantity of carbonate of potash be added to it, the alkaline liquid on boiling becomes neutral with evolution of carbonic acid, and now contains hyposulphite of potash instead of the tetrathionate and pentathionate. Dilute fuming nitric acid eliminates sulphur from the aqueous solution of the tetra-pentathionate of potash, and the presence of sulphurous acid in the liquid is detected by its odour. Chloride of barium produces no precipitate in the solution either alone or with the addition of ammonia, but after twenty-four hours a white precipitate subsides. Neutral acetate of lead produces no turbidness; but on the addition of ammonia in the cold, a white flocculent precipitate soluble in acetic acid. The protonitrate of mercury yields, both in the cold as well as at a boiling temperature, a yellow precipitate. Cyanide of mercury did not produce a yellow precipitate immediately even on the addition of nitric acid, but only after twenty-four hours. The pernitrate of mercury afforded a yellowish-white precipitate, perchloride of mercury a white precipitate. Protochloride of tin colours the solution in the course of a short time darker and darker; and at last a blackish-brown precipitate is formed, and sulphuretted hydrogen escapes. Nitrate of silver affords a yellow precipitate, which gradually becomes black; protosulphate of iron produces merely a slight opakeness, perchloride of iron no change. On the addition of chloride of barium and sulphuretted hydrogen, a turbidness results, and the odour of sulphuretted hydrogen disappears. The salt, dried under the air-pump, loses, when heated up to 212°, at first sulphurous acid and water containing sulphuretted hydrogen, then sulphurous acid, and lastly sulphur; and the residue consists of sulphate of potash, which sometimes retains a slight amount of sulphuret of potassium. The salt, dried *in vacuo*, yielded on analysis—

Potassium	24·068	2	=	979·832	23·887
Sulphur.....	44·452	9		1810·485	44·131
Oxygen.....	29·764	12		1200·000	29·241
Water	1·626	1		112·480	2·741

On ignition the tetra-pentathionate of potash is decomposed into 2 equivs. sulphurous acid, 1 equiv. water, 5 equivs. sulphur, and 2 equivs. sulphate of potash. Experiment afforded—

Sulphurous acid	20·283	2	=	802·330	19·555
Sulphur.....	24·489	5		1005·825	24·516
Sulphate of potash ..	53·602	2		2182·162	53·188
Water	1·626	1		112·480	2·741

If pentathionic acid is saturated exactly in the same manner with baryta as above with potash, there is obtained, on distilling off the acid solution, at first some sulphuretted hydrogen, and subsequently a small amount of sulphurous acid in the distillate. The concentrated liquid of the retort retains the property of precipitating the protonitrate of mercury, even after the addition of some nitric acid, permanently yellow; and it contains but a mere trace of sulphate of baryta and sulphur. On further evaporation a salt crystallized from it in prisms, which after recrystallization still had an acid reaction. According to the analysis these crystals are represented by the formula $2BaO, S^9 O^{10}, 6HO$:—

Baryta.....	35·42		2	= 1915·06	35·47	
Sulphur	34·09		9	1810·48	33·52	
Oxygen....	30·49	O 10		1000·00	18·51	31·00
Water		HO 6		1784·80	12·49	

The acid reaction and the slight excess of sulphur are owing to the salt containing a small amount of free acid.

On further evaporation of the preceding liquid nearly neutralized with barytic water, when some sulphur separated, a second crop of prismatic crystals of tetrathionate of baryta, $BaO, S^4 O^5, 2HO$, was formed. Lastly, the mother-ley deposited sulphur. The analysis of the tetrathionate of baryta gave the following results:—

Baryta.....	38·078		1	= 958·03	38·51	
Sulphur	32·461		4	804·67	32·35	
Oxygen....	29·461	O 5		500·00	20·10	29·14
Water		HO 2		224·96	9·04	

On boiling an aqueous solution of the tetra-pentathionate of baryta with an excess of barytic water, a white crystalline powder separated. It gradually dissolved after repeated treatment with boiling water, leaving a residue of some carbonate and sulphate of baryta, and the liquid exhibited the reactions of the hyposulphate of baryta.

If carbonate of lead is added to a recently prepared solution of pentathionic acid, turbid from the separation of sulphur, it dissolves with disengagement of carbonic acid. More sulphur separates, which is removed by filtration. The clear liquid yields with protonitrate of mercury a precipitate insoluble in nitric acid; sulphuric acid precipitates sulphate of lead. The solution, mixed with

an equal volume of liquid pentathionic acid, is again rendered turbid by the separation of sulphur. After this is removed the liquid becomes yellowish, reddish, and then brick-red; and finally a small quantity of a light brownish-red precipitate separates, which becomes black on drying, and is probably an oxysulphuret. When the solution of the bipentathionate of lead is heated to boiling, it remains clear, and disengages some sulphurous acid; but the solution retains the property of precipitating the protonitrate of mercury yellow until it has acquired a syrupy consistence by evaporation. At this period the liquid becomes turbid from the separation of some sulphate of lead, and acid from free sulphuric acid, while a tenacious yellow mass separates, which exhibits all the properties of the pentasulphuret of hydrogen. Owing to this decomposition, it could not be ascertained whether alcohol precipitated the tetra-pentathionate of lead undecomposed from the solution of this salt. A recently prepared solution of pentathionic acid, saturated with baryta water, affords but a very inconsiderable precipitate with neutral acetate of lead. If ammonia is added, a large amount of the salt $2PbO + S^2O^2 + 2HO$ is precipitated, which does not take up any ammonia.

All the salts of tetra-pentathionic acid previously mentioned, as also pentathionic acid, and lastly Plessis's new acid S^5O^6, afford with the protonitrate of mercury a precipitate insoluble in nitric acid. There was found in the liquid from which this yellow precipitate had been produced by the tetra-pentathionate of potash, protosulphate of mercury and free nitric acid along with the excess of the precipitant. Some protosulphate of mercury separated with the precipitate. The yellow precipitate was washed with water containing free nitric acid as long as it was rendered turbid by a solution of baryta. When dry it formed a greenish-yellow powder, resembling the protiodide of mercury, and gave on analysis—

Mercury	80·275	6 =	7954·94	79·62
Sulphur	11·167	6	1200·99	12·65
Oxygen	4·558	4	400·00	4·19
Water.....	4·000	3	337·44	3·53

This salt, $5HgS + HgO, SO^3 + HO$, belongs to the series of double compounds examined by H. Rose, of sulphur compounds with salts of mercury, which are formed by the action of an insufficient quantity of sulphuretted hydrogen upon salts of mercury. The formation of the above compound is

$$2KO, S^9O^{10}, HO + 6(Hg^2O, NO^5) = Hg^6S^6O^4 + 3(Hg^2O, SO^3) + 2(KONO^5) + 4NO^5 + xHO.$$

In the above formula the peroxide of mercury has been assumed, because it might have been formed by the presence of free nitric acid. Lime behaves towards a solution of pentathionic acid in the same manner as potash, baryta, &c. If fresh pentasulphuret of hydrogen be boiled with sulphurous acid until the odour of the latter has disappeared, the filtered liquid exhibits all the reactions of pentathionic acid.—*Archiv der Pharm.*, li. p. 259.

On the Formation of Metacetonic and Butyric Acids in the Putrefaction of Peas and Lentils. *By* Dr. R. Böhme.

Some peas and lentils were exposed with water to the sun until putrefaction had set in. The liquid was subsequently poured off the solid parts, and acidified with sulphuric acid to separate the acids formed, from the ammonia, of which the liquid contained a large amount. After distillation of the aqueous solution of the acids, the distillate was saturated with carbonate of baryta, and evaporated. Some very perfect crystals separated from the concentrated liquid, which appeared to be segments of rectangular octahedra. Alcohol extracted from the mother-ley obtained from these crystals a mere trace of an amorphous salt. The mother-ley itself dried over sulphuric acid to a vitreous amorphous mass, which yielded a white powder on pulverization. The first crystallized baryta salt of the acid from putrefied lentils was recrystallized several times from water, and furnished on analysis—

Carbon	..	23·40	25·5	6	25·4
Hydrogen	..	3·66	3·6	5	3·5
Baryta	54·1	52·90	52·2	1	54·2

The substances employed in these analyses were samples from different crops of crystals. As the numbers show, the results approach the composition of metacetonic acid, which in fact forms the principal constituent of the salt, but still contaminated with other substances. Among these is butyric acid, which was detected by its odour in all the salts obtained, and constituted the amorphous salt in the mother-ley. The metacetonic acid was obtained purer by recrystallizing its silver salt, to prepare which the above baryta salt was precipitated with nitrate of silver. A granular white precipitate separated, which became brown in water near the boiling-point, and then dissolved with the elimination of some metallic silver. By this treatment it appears that the slight impurities of the metacetonic acid are destroyed, and the latter obtained in a purer state. As the solution cools, the silver salt separates in a crystalline granular state and faintly brown; it can be dried in the dark without experiencing any perceptible change. But even in this state the salt still smelt faintly of butyric acid; it was dried for some time at 104° F., and analysed; the results agree very closely with those calculated from the formula of metacetonic acid:—

Carbon	20·6	6	19·6
Hydrogen	2·9	5	2·7
Oxygen	16·5	4	17·6
Silver	60·0	1	60·1

The distillate from the peas saturated with carbonate of baryta furnished a residue almost entirely soluble in alcohol; the baryta salt crystallized from this solution in pearly scales. When sulphuric acid was poured over it, it disengaged a strong odour of butyric acid; and when mixed with sulphuric acid and alcohol, decidedly that of butyric æther. The quantity of the salt obtained, however,

was too small to purify it by recrystallization; and the butyric acid in the salt, as exhibited by the analyses, still contained a large amount of impurities. The mother-ley from this salt dried over sulphuric acid to a vitreous mass, which was a mixture of several salts. Experiments to separate them by combining them with different bases, led to no result. One combustion made with the substance, dried at 212°, afforded 18·1 per cent. carbon, 2·7 hydrogen, and 56·6 baryta.—*Journ. für Prakt. Chem.*, xli. p. 277.

On the Chloride of Titanium and some other Combinations of Titanium. *By* M. Ebelmen.

The study of some minerals containing this metal has of late attracted the attention of chemists to the oxides of titanium, of which titanic acid is the sole one the constitution of which has been ascertained with certainty. Berthier has shown that titanic acid becomes black at a very high temperature, losing from 5 to 6 per cent. of oxygen; and, on the other hand, it is known that solutions of titanic acid in other acids are coloured blue by the action of some metals placed in them, and in this state afford blue or black precipitates with ammonia, which after some time again pass into white titanic acid with evolution of hydrogen. Fuchs, by the investigation of sphene, and Rose, from the examination of titaniferous iron, were led to admit the titanium in the above minerals to be in the state of an oxide $Ti^2 O^3$. The following researches show that such an oxide and the corresponding chloride do really exist.

Sesquichloride of Titanium was obtained by heating the perchloride $TiCl^2$ to redness in a current of hydrogen. The perchloride was contained in a tubulated retort, through the tubulus of which the hydrogen gas was conveyed from the drying apparatus, after having been purified by passing through a solution of silver, into the retort. The neck of the retort was continued into the porcelain or glass tube where the heat was to be applied; and when the contents of the retort were gently heated, vapours of the perchloride of titanium were propelled with the hydrogen through the tube. A suitable recipient was adapted to the other end of the tube, in order to collect a portion of the perchloride, which, whatever the proportion of hydrogen employed, was constantly carried over partially undecomposed. The sesquichloride which is formed is far less volatile, and is deposited on those portions of the tube just beyond the furnace. By applying a gentle heat to this part, a current of hydrogen being kept up until the apparatus had cooled, and after all the substance in the retort had been volatilized, the new product could be obtained free from any adherent perchloride. It was immediately sealed up in dry glass tubes. This new chloride of titanium forms large, dark violet, shining scales, which readily become altered. When heated with access of air, it is immediately converted into titanic acid with evolution of dense vapours of the perchloride. The same products of decomposition appear to be gradually formed at the ordinary temperature; for when the new sesquichloride has been preserved for some time in a somewhat capacious vessel, it becomes

white on the surface, and fumes when exposed to a moist atmosphere. In the pure state the sesquichloride deliquesces in a moist atmosphere to a liquid without fuming; it dissolves in water with evolution of heat; the solution has a violet-red colour, and is gradually decolorized by exposure to the air, a deposit of titanic acid being formed at the same time. On evaporating this solution to dryness, muriatic acid escapes and a blue oxychloride remains. In analysing this product, a certain quantity was weighed off in a perfectly dry flask, dissolved in water, and a few drops of nitric acid added to it, which quickly decolorized the solution with disengagement of nitric oxide. In general a few particles (titanium, blue oxide of titanium) remained undissolved, the weight of which was subtracted from that of the substance employed. The titanic acid formed was then precipitated with ammonia, the precipitate washed with cold water, and the muriatic acid in the filtered liquids determined with solution of silver. The author obtained in this manner—

Titanium	32·3	31·7	31·6	2	606·2	31·3
Oxygen	67·7	67·2	..	3	1327·8	68·7

Considering the great instability of the product examined, owing to the access of air, the differences between the found and calculated results will appear very slight; moreover, the following combinations further confirm the formula above assumed for this sesquichloride. It is very probably converted into the sesquimuriate on solution in water. Ammonia produces in this violet solution a dark brown precipitate, which soon becomes black in the air, then blue, and at last white, while hydrogen gas is evolved. This brown precipitate, which is first produced, is undoubtedly the hydrated sesquioxide; and as it only becomes blue after a certain quantity of hydrogen has been disengaged, it is evident that the blue oxide must be intermediate between the sesquioxide and acid. Carbonated alkalies produce the same reaction as the caustic, only that the carbonic acid is evolved along with hydrogen. Sulphuretted hydrogen has no action upon the solution; sulphuret of ammonium precipitates the brown hydrated sesquioxide, which behaves as above described. The ferrocyanides produce a brownish precipitate, which soon becomes green, and is instantly turned green by chlorine. The solution of the sesquichloride of titanium is one of the most powerful reducing agents. At a boiling temperature it separates sulphur from sulphurous acid, reduces gold, silver and mercury from their solutions, throws down protochloride of copper from solutions of the oxide, and converts solutions of persalts of iron into protosalts, from which latter ammonia precipitates white titanic acid; while if the access of air be prevented, protoxide of iron remains in solution. A very minute quantity of the sesquichloride of titanium suffices to render soluble a large amount of the violet insoluble perchloride of chromium. The above-described property of the brown hydrated sesquioxide, of decomposing water to form titanic acid, was turned to account in ascertaining the composition of the violet sesquichloride. For this purpose a small glass tube, containing a weighed quantity of the sesquichloride of titanium, was entirely filled with water, placed

under a graduated cylinder filled with mercury and solution of ammonia, and left undisturbed for twenty-four hours, at the end of which time the brown precipitate had become perfectly white. The quantity of gas given off by 0·774 grm. of the sesquichloride amounted, after reduction of the barometer and thermometer, to 55·9 per cent. According to the formula $TiCl^3$, it should give 53·3.

Protochloride of Titanium and Titanium.—In preparing the sesquichloride as above described, it is not the only product which is formed; metallic titanium is found in the reduction-tube mixed with the chlorine compound, which is not acted upon by water, but dissolves in ammonia. From its small quantity it could not be further examined; but it is very probably the protochloride. During the whole of this operation the same products are always obtained from a red to a white heat, but the higher the temperature the more metallic titanium.

Sesquioxide of Titanium.—When titanic acid is heated in a perfectly dry current of hydrogen, it experiences a very perceptible decrease in weight. The least trace of humidity in the gas prevents this. For these experiments I employed the ignited acid, which had been precipitated from the perchloride of titanium with ammonia. It was weighed in a platinum vessel, and this ignited in a porcelain tube in hydrogen until the loss in weight remained constant. It lost in this manner 0·086 oxygen, and became converted into dark black sesquioxide, which requires, according to the formula $Ti^2 O^3$, 0·095 oxygen to form acid. In a second experiment, 0·485 acid lost 0·045 oxygen; the amount required by theory is 0·048. These results show that the composition of the black oxide undoubtedly corresponds to that calculated according to the formula $Ti^2 O^3$. This black oxide is very difficult to oxidize any higher. It becomes white by roasting at a very high temperature. Muriatic and nitric acids do not attack it; sulphuric acid dissolves it to a violet liquid. From the circumstance that titanic acid is certainly reduced by hydrogen, which hitherto has not been admitted, it is evident that the analysis of the titanate of iron, in which the mixture of titanic acid and peroxide of iron was exposed in a current of hydrogen, under the supposition that the iron alone was reduced, must be erroneous.

Sesquisulphate of Titanium.—When the sesquichloride of titanium is dissolved in sulphuric acid, and the liquid concentrated over lime *in vacuo*, the salt separates in indistinct crystalline masses, which even on recrystallization do not assume a more perfect form. This salt is very deliquescent; its solution is violet; it is decolorized by boiling with access of air, and deposits white titanic acid. The sesquisulphate behaves towards reagents like the sesquichloride. The analyses of this salt led to no exact result; but the amount of sulphuric acid in the salt always exceeded that corresponding to the neutral salt $Ti^2 O^3$.

Sulphuret of Titanium.—Hitherto we have only been acquainted with the sulphuret prepared by Rose, who procured it by heating titanic acid to redness in the vapour of sulphuret of carbon, and which Berthier likewise obtained by fusing oxide of titanium with

carbonate of soda and sulphur. Rose's sulphuret contains 49·17 per cent. titanium and 50·33 sulphur; Rose regards it as corresponding to titanic acid; if with Rose we adopt the atomic weight 303·1, as deduced from the perchloride of titanium, the above results correspond rather to the formula $Ti^2 S^3$ than to that of the bisulphuret of titanium; it requires 50·2 titanium and 49·8 sulphur. The author found, in very numerous experiments in which titanic acid was heated to redness in the vapour of sulphuret of carbon, frequently an approximation to the latter formula; but in the determination of the sulphur and the titanium there was always a small loss, occasioned by the presence of some oxygen which could not be removed by the sulphuret of carbon. The colour of the sulphuret obtained was sometimes black and sometimes dark green; consequently the product is not of constant composition.

Bisulphuret of Titanium.—This compound was obtained by passing sulphuretted hydrogen through a retort in which chloride of titanium was heated to nearly its boiling-point, and thus charged with the vapours passed through a faintly incandescent tube. The inside of the tube was coated with bisulphuret of titanium, while muriatic acid escaped. This compound is obtained thus in the form of broad, crystalline, brass-yellow scales, with metallic lustre, and which may be rubbed like mosaic gold upon the skin, forming a very adherent gilt coating. It is altered by exposure to the air after some time, and diffuses the odour of sulphuretted hydrogen. It is insoluble in muriatic and in dilute sulphuric acid; *aqua regia* dissolves it without any perceptible residue, while that prepared with sulphuret of carbon leaves a considerable residue. When heated, it burns to titanic acid, retaining its form. For analysis, it was dissolved in *aqua regia*, the titanic acid precipitated with ammonia, and the sulphuric acid with chloride of barium:—

Titanium	44·12	44·05	1 =	303·1	43·1
Sulphur.....	56·40	..	2	400·0	56·9

Upon the bottom of the retort which contained the chloride of titanium is found an olive-green substance, which when rubbed acquires metallic lustre, and is nothing less than the bisulphuret. The reaction begins therefore below the boiling-point of the perchloride of titanium.

The probability that the sulphur compounds of some other metals whose chlorides are volatile might likewise be obtained in the same manner, was confirmed in one experiment, in which perchloride of tin was substituted for the perchloride of titanium. A mosaic gold of the greatest beauty was formed when the temperature of the tube in which the gases were heated did not completely reach that of red heat. Calculating the results obtained according to the equivalent recently determined by Pierre, Ti = 314·7, we obtain for the salts above described—

Titanium....	32·76	2	32·14	Titanium	44·70	1	44·03
Chlorine	67·60	3	67·86	Sulphur	56·40	2	55·97

Ann. de Chim. et de Phys., xx. p. 385.

ANALYTICAL CHEMISTRY.

On the Estimation of Chromium in its Compounds by Carbonic Acid. *By* H. Vohl.

The method hitherto employed to determine chromium in its compounds in the form of oxide of chromium is connected with several difficulties, and does not always furnish accurate results. Having been long occupied with an investigation of the compounds of chromium, I was very desirous of discovering a method by which this metal, whether it occurred in the form of acid or oxide, might be determined more accurately and readily than hitherto. The behaviour of chromic acid towards oxalic acid led me to estimate it by carbonic acid. When chromic acid is mixed with oxalic acid, the former behaves like a superoxide, parting with oxygen to the oxalic acid to form carbonic acid, and being at the same time reduced to oxide of chromium,

$$2(CrO^3) + 3(C^2O^3) = Cr^2O^3 + 6CO^2.$$

For each equivalent of chromic acid 3 equivs. carbonic acid are formed, or 66 parts by weight for 50·31 parts of chromic acid. If the chromium is estimated as oxide, there is obtained, when it is in the form of chromic acid, 26·31 parts by weight of oxide of chromium for 50·31 parts of chromic acid. Every error made in the estimation of the oxide is increased on calculating the chromic acid from it; this is not the case on estimating it from the carbonic acid.

To determine the amount of carbonic acid, I employed the apparatus described by Will and Fresenius for the analysis of manganese*. If merely the chromium has to be determined, any oxalate may be taken; but if the alkalies are likewise to be determined in the residuary liquid, oxalate of ammonia or baryta is employed. The analysis is very simple; when the chromium exists in the compound in the form of acid, the salt is taken then just as it is, and the process is precisely the same as in the analysis of manganese. If the salt is a chlorochromate, before allowing the sulphuric acid to pass over, oxide of mercury must be mixed with the salt to prevent the elimination of chlorine or muriatic acid; after the operation the amount of chlorine can be determined from the perchloride of mercury by nitrate of silver, and the quantity of chlorochromic acid contained in the salt calculated from it.

The determination is less simple when the salt contains oxide of chromium. In the first place, the oxide must be converted into chromic acid, and this is best effected in the following manner:—The salt to be examined is dissolved in water, and caustic potash added to it until the whole of the hydrated oxide of chromium has redissolved; upon which, keeping the solution cold, chlorine is passed into it until the green colour is changed into a yellowish-red one;

* Figured at p. 53 of the second volume of this Journal.

an excess of potash is now added to this liquid, which is evaporated in the water-bath, and heated to faint redness in a platinum crucible. The whole of the chlorate of potash is decomposed, chromate of potash and chloride of potassium remaining; these are dissolved, transferred with oxide of mercury into the apparatus, and the operation conducted as with chromates. The amount of oxide of chromium can be easily calculated from the quantity of carbonic acid which has escaped. 6 equivs. of carbonic acid are set free for each equivalent of oxide of chromium:

$$Cr^2O^3 + O^3 = 2CrO^3$$
$$2(CrO^3) + 3(C^2O^3) = Cr^2O^3 + 6CO^2.$$

In analysing a salt in which both chromic acid and oxide of chromium occur, two determinations must be made. In the first place the carbonic acid is determined, which the salt yields as it is, and the chromic acid calculated from the amount; upon which the liquid is treated as a salt of the oxide, the quantity of carbonic acid first obtained subtracted from that last obtained, and the amount of oxide of chromium calculated from the difference.

This method of estimating chromium will render it possible for every one to submit to analysis those compounds of chromium which occur so frequently adulterated in commerce.—Liebig's *Annalen*, Sept. 1847.

On the Analysis of the Oxygen Compounds of Sulphur.
By J. Fordos *and* A. Gélis.

The determination of the oxygen in the lower acids of sulphur is somewhat difficult; the process hitherto used is a modification of that employed by Dulong in the analysis of the acids of phosphorus; it is however difficult, tedious, and requires skilful hands to lead to accurate results. In the researches with which we have been engaged, we required a quicker and more accurate process. After numerous experiments we found in the use of standard solutions of hyperchlorites a method of analysis remarkable from its simplicity and accuracy, and which promises to be of considerable use in the analysis of the lower oxides of sulphur, phosphorus, arsenic, &c. All the acids of sulphur are completely oxidized in the cold by the hyperchlorites without it being requisite to use an excess of the reagent. Hyposulphuric acid forms the sole exception.

The estimation of the oxygen in the acids of sulphur is performed like a chlorometric assay. After having determined the strength of the solution of hypochlorite by means of arsenious acid, the latter is replaced by a weighed quantity of the salt to be analysed. We generally operate upon 1 decigrm. of substance dissolved in about 100 grms. of water. The liquid is acidified, in order to render the reaction more quick, and to indicate the moment when it has terminated; in general, however, this is known by the odour of chlorine; moreover, recourse may be had to indigo, as in chlorometric assays.

The number of equivalents of chlorine absorbed represents the number of equivalents of oxygen which the sulphur acid required to be converted into sulphuric acid. We can also advise the use of hyperchlorites in determining the total amount of sulphur in a mixture of the acids of sulphur, and even in the isolated acids. The hyperchlorites possess decided advantages over the oxidizing agents usually employed; it must be merely borne in mind that it is requisite to act upon very dilute solutions.—*Comptes Rendus*, Nov. 2, 1847.

New Method of estimating the Amount of Soda in Crude Potash. *By* M. Pagenstecher.

The following is a simple and ready method of detecting any adulteration of potash with soda. The usual impurity in unsophisticated potash is generally sulphate of potash (and chloride of potassium); a saturated solution of sulphate of potash is capable, like many other salts, of still dissolving a large amount of sulphate of soda. Upon this property is based the method of examination adopted by M. Pagenstecher. A certain weight, about half an ounce, is mixed with water, and sulphuric acid added to it until the liquid has an acid reaction; it is then evaporated to dryness, the residue ignited and weighed. The powdered saline mass is well agitated in a graduated cylinder with six times its weight of a concentrated solution of sulphate of potash, the liquid drawn off from the sediment with a siphon, and the same quantity of the solution of the sulphate of potash again poured over the residue. After some time the residue is brought upon a weighed filter, the funnel covered during filtration, the filter when the liquid has drained off weighed moist, and then after being dried at 212°, the difference is the evaporated water of the solution of the sulphate of potash, the degree of concentration of which is known. It is known therefore how much of the salt was dissolved in the evaporated water; this quantity is subtracted from the weight of the saline residue. If the potash was free from soda, the weight of the sulphate of potash now remaining must be the same as that first obtained. If the potash contained soda, this has been removed as sulphate of soda, and the weight of the first saline residue has been reduced. From the loss the amount of the soda present can be calculated; if the loss = V, the amount of soda

$$887{\cdot}2\ (NaO\ SO^3) : 662{\cdot}2\ (NaO\ CO^2) :: V : X.$$

It should however be observed, that when soda is used to adulterate potash, a kind is employed that contains about 20 per cent. sulphate of soda. Before making the weighings it is well to take the specific gravity of the filtered solution of the sulphate of potash; if it is the same as before it can have removed nothing, and if it has taken up sulphate of soda its density has naturally been raised.—*Mittheilungen der Naturf. Gesells. in Bern.*

CHEMICAL PREPARATIONS.

On the Preparation of Chloroform. By M. Soubeiran.

The following is the process which I now employ for preparing this substance, the publication of which, although perhaps somewhat premature, I shall not regret if it may have assisted in admitting some destitute sick to an earlier participation in the beneficial effects derived from anesthesia by chloroform.

I take 10 parts of commercial chloride of lime of about 90°, mix it carefully with 60 parts of water, transfer the lime-milk which results into a copper still, which should not be filled more than two-thirds, add 2 parts of alcohol of 0·85, and adapt the head and the receiver; when the joints have been well-cemented, a brisk fire is kept under the apparatus. At about 176° a violent reaction ensues, which raises the mass, and would cause it to pass into the receiver if the fire were not quickly removed; this is the only difficult part of the operation. Its approach is indicated by the temperature of the neck of the still. When this has become much heated at its most distant end, before any products of distillation have begun to appear the firing is removed. A few moments afterwards distillation begins, and proceeds rapidly of itself until almost complete. As soon as I observe the action to become slow, I restore the firing to assist it. It is very soon terminated, which is easily known from the liquids which pass over no longer possessing the sweet taste of chloroform. The distillate is composed of two strata; the lower one is dense and slightly yellowish; it consists of chloroform mixed with alcohol and contaminated with a little chlorine; the upper stratum is a mixture of water, alcohol and chloroform, and in the course of twenty-four hours deposits a quantity of the latter product.

The chloroform is separated by decantation, agitated with water to wash it, and then with a weak solution of carbonate of soda to remove the chlorine; it is then rectified over chloride of calcium in the water-bath. For medical purposes I have considered it quite superfluous to submit it to a further rectification over sulphuric acid. The upper stratum of the product from the distillation, and the waters used in washing are united, diluted with more water, and distilled in the water-bath. The chloroform soon passes over, carrying with it a little water and spirit. It is purified as above described.

The principal difficulty in the preparation of chloroform is the necessity of working with very dilute chloride of lime, from fear of other bodies originating, especially of acetic products, which it would be almost impossible to separate. Hence the necessity of operating in vessels of large dimensions, although working with very small quantities of alcohol. It must moreover be remembered that chloroform appears to be only a secondary product. In the violent reaction which ensues between the hypochlorite of lime and alcohol, there is always much less obtained than theory would lead us to expect. Fortunately each operation occupies but little time, and

several distillations may be made one after the other in the course of a day.

My first efforts were restricted to determine the most advantageous proportions of chloride of lime, water and alcohol. I have likewise made some experiments to ascertain the influence of a longer or shorter contact, and I am induced to think that the operation is the more productive the quicker it is effected. I believe that it is very advantageous to mix the pulverized chloride of lime in hot water, in order that it may more rapidly attain the temperature of 176° requisite for the production of chloroform.

A great deal of the chloroform sold at first was not sufficiently pure. I may observe, that notwithstanding its apparent fluidity it is very heavy, and this furnishes a ready method of ascertaining its purity. By mixing equal parts of concentrated sulphuric acid and distilled water, a liquid is obtained, which on cooling indicates 40° on the areometer (spec. grav. 1·35). One drop of chloroform poured into this liquid sinks to the bottom. This is a very simple test and easily practised, which I hope will prevent the sale of chloroform mixed with alcohol.—*Comptes Rendus*, Nov. 29, 1847.

Observations on the Preparation of the Oxide of Gold (Auric Acid). *By* L. Figuier.

The oxide of gold is at present extensively used in the arts, owing to its substitution for the cyanide of gold in the liquids employed in electro-gilding. This has induced me to determine by comparative experiments which of the processes employed for the preparation of this oxide is that which offers the greatest advantages. Three processes have been described. The first, proposed by J. Pelletier, consists in treating a solution of the chloride of gold with calcined magnesia, and subsequently decomposing the aurate of magnesia thus formed with dilute nitric acid. The second process, which I have described in my memoir on the oxides of gold, consists in decomposing a solution of chloride of gold with carbonate of soda and boiling. The amount of carbonate of soda should accurately suffice to saturate the acid without the liquid acquiring an alkaline reaction. In the third process, which I have recently proposed, the oxide of gold is obtained by treating in the cold a solution of chloride of gold with chloride of barium to which some caustic potash has been added. A precipitate of aurate of baryta is formed, which is decomposed with nitric acid.

With a view of comparing these three processes, I have determined the quantity of oxide which each is capable of yielding with the same weight of gold. 10 grms. of gold furnished by Pelletier's process 9·08 grms. oxide, well dried by long exposure to the air. With carbonate of soda 10 grms. of gold yielded 10·48 of oxide; and the same quantity of metal, treated with chloride of barium and potash, gave 11·72 oxide. This last process is consequently the most advantageous as regards the amount of product, but it is likewise that which yields the purest oxide. The oxide of gold obtained

by carbonate of soda retains a certain quantity of alkaline carbonate, which cannot be removed by washing. On decomposing a little of the oxide by heat, and exhausting the gold with hydrochloric acid, the liquid leaves on evaporation a residue of chloride of sodium, while the oxide prepared with chloride of barium affords no appreciable residue when treated in the same manner, and the solution is scarcely rendered turbid by sulphuric acid. The process is moreover so rapid and simple of execution, that on this account alone it appears to me preferable to the two others, especially to Pelletier's, which, as is well known, is long and tedious on account of the large bulk of the magnesian precipitate and of the time required for washing. I think it may be useful therefore to describe this new process at some length, especially as the only account of it hitherto published is a brief notice in the new edition of Soubeiran's 'Traité de Pharmacie':—1 part of gold is dissolved in 4 parts of nitromuriatic acid, the solution evaporated to dryness, redissolved in water, which leaves a slight residue of metallic gold and of protochloride, which is redissolved with a little nitromuriatic acid. This solution is again evaporated to dryness, and redissolved in water. The solution of the chloride of gold, which is thus obtained quite free from acid, is mixed with pure potash (perfectly free from chloride) until it has a strong alkaline reaction upon curcuma-paper. It immediately becomes turbid; the solution is then mixed with chloride of barium, which instantly yields a canary-yellow precipitate of aurate of baryta. The addition of chloride of barium is discontinued when the precipitate begins to appear slightly white, which shows that the whole of the oxide of gold being precipitated, the alkali has begun to act upon the baryta of the chloride of barium. The supernatant liquid is colourless; consequently the metal is almost entirely precipitated from its solution. The aurate of baryta thus obtained is very heavy, and easily washed by decantation. It is washed until the waters cease to be precipitated by sulphuric acid; the aurate of baryta is then treated with nitric acid diluted with water, which sets the oxide of gold free. It is requisite to heat the liquid to boiling, and to keep it at this temperature for some minutes, in order to decompose the last traces of the baryta salt. On washing by decantation until the water no longer reddens litmus-paper, the oxide is obtained pure.

By whichever process the oxide of gold is obtained, particular attention must be paid to the mode of drying it. The temperature of boiling water, which is sometimes used, frequently reduces a part of it. It may be dried *in vacuo* or under a bell-glass over sulphuric acid; but the most simple plan is to press it between folds of blotting-paper, and to expose it to the air protected from the light.

I may briefly notice, before concluding, the best method of obtaining the gold from the liquids resulting from these operations. The liquids resulting from washing the aurate of baryta must not be mixed with those obtained in washing the oxide. The first contain far more gold. They are concentrated by evaporation, and the baryta precipitated by sulphuric acid; the liquid, after standing, is decanted, and a solution of protosulphate of iron added to it, which

precipitates the whole of the gold. The waters derived from washing the oxide are also evaporated and precipitated by sulphuric acid; but they must not be treated immediately with protosulphate of iron, on account of the action which the free nitric acid they contain exerts upon this salt. After precipitation with sulphuric acid, the liquid is decanted and evaporated to dryness, and the small residue obtained treated with nitromuriatic acid. This solution is evaporated nearly to dryness to expel the nitric acid, then diluted with water, and treated with sulphate of iron.—*Journ. de Pharm.*, Dec. 1847.

On the Preparation of the Citrate of Magnesia Lemonade. *By* M. Massignon.

This medicine, which was recommended by M. Delabarre, may be simply and advantageously prepared in the following manner:—To obtain a clear solution, pure carbonate of magnesia is prepared by precipitating a filtered boiling solution of sulphate of magnesia with carbonate of soda. 5 grms. of this in the dry state are then formed with water into a milk, which is poured into a strong glass bottle which is nearly filled with water, and upon this 7 grms. of citric acid in crystals added, and the bottle quickly and firmly corked. It need not be stated that different syrups may be introduced to improve the taste before adding the acid.—*Journ. de Pharm.*, xii. p. 31.

On the Preparation of Strychnine. *By* M. Molyn.

8 lbs. of the powdered fruit of *Strychnos Nux vomica*, are mixed with the same quantity of water, so as to form a thick paste, which is then exposed to a temperature of 68°–77°. In the course of a few days a violent fermentation sets in, which is generally finished in about eighteen to twenty days. It is now passed through a hair-sieve, pressed, the residue boiled twice or three times with water, and the united liquids evaporated down to 12 quarts. Upon this 9 oz. of calcined powdered lime are added, the whole left quiet for six to eight hours, and the liquid separated from the precipitate by pressure; it is then mixed with sulphuric acid, the eliminated sulphate of lime removed, and the liquid evaporated to 2 quarts. 1 oz. of lime is now added to it, and the course repeated as above described. The precipitate formed is submitted to great pressure, and united with the previous one. The dried precipitate is now digested with 2 quarts of spirit of 0·935 spec. grav., which dissolves out brucine and colouring substance; from this solution strychnine is likewise obtained by crystallization. The last precipitate is digested repeatedly with 6 quarts of spirit of 0·838; the tincture is filtered, and four-fifths of the spirit removed by distillation. In the course of one or two days the strychnine separates as a white crystalline powder, which is washed several times with alcohol of 0·935 to remove any adherent brucine, and is obtained perfectly pure by recrystallization. —*Journ. de Chim. Méd.*, vol. iii. p. 507.

New Method of preparing Chloride of Lime. By C. H. Mène.

The method which I propose for producing chloride of lime furnishes it always pure, almost instantaneously, and at far less expense than that usually employed. I take what is commonly called *slaked lime*, and pour upon it water saturated with chlorine. The chlorine is absorbed the moment the liquid comes into contact with the lime; if the supernatant water is immediately decanted, and the lime remaining at the bottom of the vessel saturated by frequent repetition of the treatment with chlorine water, perfectly pure chloride of lime is obtained.

To preserve this product, it should be exposed for a few instants in a vessel to a gentle heat, to drive off the water which the lime may have absorbed. The chloride of lime thus obtained is dissolved in water, thrown upon a filter, when it passes, leaving scarcely any residue, according as the lime was more or less pure. However, as the chloride of lime is very rarely used in the solid state, it is scarcely necessary to go through this series of operations.

This process has the advantage of being not only rapid and œconomical, but admits of turning to account the chlorine water produced in the manufacture of *Eau de Javelle* or in soap-boiling.—*Comptes Rendus*, Nov. 22, 1847.

Candied Pills.

Dorvault recommends that the pills be coated with gum, by which means they acquire a candied aspect, and present the same advantages as the gilt pills did formerly. After the pills are rolled, they are to be shaken in a spherical box with 1 or 2 drops of simple syrup, so as to render them moist. They are then mixed gradually by shaking with powdered gum, either by itself or with oleo-saccharum, until they cease to take up any more, when they are dried. If it be required to render the coating perfectly transparent, some starch is added to the powdered gum.—Buch. *Rep.*, xliii. p. 380.

On the Adulteration of Succinic Acid. By Prof. Wackenroder.

The author draws attention to the sophistication of commercial succinic acid with tartaric acid soaked in oil of amber. A quantity procured from Frankfort-on-the-Maine consisted solely of tartaric acid mixed with oil of amber.—*Archiv der Pharm.*, l. p. 280.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Peculiar Constituents of the Fruit of Anacardium.
By Dr. STÆDELER.

THE fruit known by the name of Cashew nuts and noix d'acajou, which appear to have formerly been officinal, but are now no longer met with in commerce, are derived from a tree which occurs in South America and the West Indies, the *Anacardium occidentale*, L., *Cassuvium occidentale*, Lam., which belongs to the family of the *Cassuviæ* and to the Enneandria monogynia of the Linnæan system. They are kidney-shaped, and of a brownish-yellow, somewhat variegated colour, by which they are easily distinguished from those nuts which are still frequently met with among druggists by the name of Eastern Anacardium; the latter are blackish-brown and cordate.

The nut incloses a kernel, which in taste exactly resembles sweet almonds, and contains a sweet fatty oil; the pericarp, which consists of two lamellæ about a line apart from each other, incloses in its intermediate cellular cavities a brown balsam-like substance, which is oily at the ordinary temperature, has a burning acrid taste, and produces inflammation of the skin.

The fruit of *Anacardium* were first examined by Cadet, who found in them gallic acid, and noticed the acridity of the substance contained in the pericarp; but he was not of opinion that it could be employed with success in medicine. They were subsequently examined by De Mattos, who found in the shells, besides the acrid body, which he calls resin, a large quantity of gallic acid, tannin, an extractive substance, a gum-resin (*gomme d'acajou*), and a green colouring principle. His attention was especially directed to the medicinal action of this resin, but he extolled its properties so extravagantly, that it was apparently soon forgotten. He employed it both externally as a vesicative, and inwardly in doses of 2 grs. as a drastic, and in doses of from a quarter to half a grain as a gentle stimulant. Similar results were obtained by two French physicians, MM. Eindral and Bully.

To obtain this body, the nuts, freed from the kernels and crushed, were exhausted with æther as long as this removed anything, the æther distilled from the clear solution, and the residue repeatedly washed with water to remove a small quantity of tannic acid which was

mixed with it. In this manner a reddish-brown liquid was obtained, which possessed scarcely any smell, and resembled Peruvian balsam; it formed about one-third the weight of the shells. At the ordinary temperature it is of an oily consistence, is very easily dissolved by æther and by alcohol, and the solutions strongly redden blue litmus-paper. No volatile product was obtained on distilling it with water. When treated with dilute acids, it parts with a small quantity of ammonia. On spontaneous evaporation of the æthereal or alcoholic solution at a low temperature, the residue solidifies to a tissue of ramified crystals of a white colour, from which a reddish oily liquid separates.

It produces upon the tongue at first an astringent taste, and then a burning and reddening. To ascertain its effects upon the skin, I made the following experiment:—A spot of about one square inch upon the lower part of the breast was spread over with the balsam, and a piece of blotting-paper, which had been moistened with it, placed over it. In the course of a quarter of an hour a slight burning was perceptible, which rapidly increased, and appeared to have attained its greatest energy in about half an hour. The skin beneath the paper had become whitish, surrounded by a red circle. As the inflammation ceased and no further inconvenience was felt, the paper was allowed to remain for about three hours. The skin was covered with small vesicles, which increased considerably in size during the night, without however attaining to the size of those usually produced by cantharides plaster. The place was dressed with linen smeared with tallow; it not only healed very slowly, but the after-effects appeared to continue for a very long time; and after an abundant secretion of pus, the wound was from ten to fourteen days in healing.

A second experiment, made with balsam which had been treated with dilute muriatic acid, afforded the same result.

The muriatic extract left on evaporation crystals, which on examination proved to be chloride of ammonium. Since the balsam which had been treated with muriatic acid contained no more nitrogen, it is evident that its effects cannot be ascribed to any nitrogenous organic compound; they are owing to a substance which is oily even at a low temperature, and forms about 10 per cent. of the mixture, the greater part of which consists of a crystalline substance which has no effect upon the skin. This latter body belongs to the fatty acids, but it is not combined either with the oxide of lipyle or any other body occupying its place. I propose for this fatty acid the name of *anacardic acid*, and for the active constituent that of *cardol*. The balsam, moreover, contains a small quantity of some colouring substances, which appear to result from the decomposition of the cardol, and will be treated of when that substance is described.

Anacardic Acid.—To separate the anacardic acid from the cardol, the mixture, extracted with æther and washed with water, is dissolved in from 15 to 20 parts of alcohol, and the solution digested with recently-precipitated hydrated oxide of lead, which combines with the

acid and the products of decomposition of cardol, which also appear to possess acid properties; the liquid loses its reaction upon blue test-paper and retains the cardol in solution. The precipitate is collected on a filter, and washed with strong alcohol until the drops falling into water no longer produce any turbidness. The lead salt is then mixed with water, decomposed with sulphuret of ammonium, and the solution of anacardate of ammonia decanted from the sediment of sulphuret of lead. The latter is washed once or twice with a little water, and the united liquids decomposed with dilute sulphuric acid, when the anacardic acid separates in soft adherent masses, which soon solidify in the cold. They are repeatedly washed by decantation with cold water and dissolved in alcohol, when in general a little sulphur and sulphuret of lead remain. The moderately concentrated solution, which is still coloured, is mixed with water until a slight permanent turbidness is perceptible, upon which it is heated to boiling, and basic acetate of lead added by drops to it until the colouring substance, along with a considerable quantity of anacardic acid, subsides in the form of dark oily drops. In the course of twelve hours the liquid is clear and nearly colourless; it is decanted and the residue exhausted with alcohol, which leaves a nearly black lead compound behind, soluble in æther. The alcoholic extract is of a red colour; it is again mixed with water until the appearance of slight opacity, and treated while boiling with basic acetate of lead as before, when dark drops of resin subside. The clear liquid is united to that previously obtained, and the residue, if it appear worth while, treated in the manner described. To remove the last traces of colour, the liquids are boiled for a short time with recently-precipitated carbonate of baryta, when in the course of twelve hours a brown stratum is deposited upon the baryta, and the solution of the anacardic acid is perfectly colourless. Carbonate of baryta does not exert this decolorizing property before the treatment with basic acetate of lead.

The clear solution of the anacardic acid is now mixed with strong alcohol, and while boiling precipitated with a neutral alcoholic solution of acetate of lead. The addition of alcohol is requisite to facilitate the washing, as otherwise, instead of forming a white powder, the precipitate is flocculent. This, after washing, is suspended in alcohol, and decomposed with sulphuric acid or sulphuretted hydrogen, when, after removing the alcohol by distillation and mixing with water, the anacardic acid separates as an oily liquid, and as soon as the last traces of alcohol have evaporated spontaneously, solidifies to a crystalline mass. The acid separated with sulphuretted hydrogen crystallizes with greater difficulty, and moreover a peculiar disagreeable odour adheres to it, which even accompanies it in some of the salts, on which account the separation with sulphuric acid deserves the preference.

Anacardic acid forms a white crystalline mass, which melts at 79° F., and is some time before it returns to the crystalline state. It is void of smell, and has a faint aromatic burning taste, but does not blister the skin. It may be heated to 302° without affording con-

densible products; but even at 212° it evolves a peculiar odour, without however experiencing any perceptible alteration in weight. At 392° it is decomposed into a very mobile, oily, colourless liquid, which was not further examined. It burns with a bright smoky flame, and produces a greasy stain upon paper. It is heavier than water. On long exposure to the air it deliquesces, and diffuses an odour perfectly similar to a rancid fat; and this occurs more rapidly with the acid separated by sulphuretted hydrogen than with that prepared with sulphuric acid. It dissolves readily in æther and alcohol, and the solutions strongly redden blue litmus-paper.

The crystallized acid afforded on analysis the following results:—

Carbon	75·06	75·02	75·07	44	= 75·04
Hydrogen	9·17	9·19	9·19	32	9·07
Oxygen	15·77	15·79	15·74	7	15·89

From the analyses of the lead and baryta salts it was evident that 2 atoms of water may be replaced by bases; the formula of the anhydrous acid is consequently $C^{44} H^{30} O^5$, and its atomic weight* 4179·68; that of the crystallized acid $C^{44} H^{30} O^5 + 2HO$, and its atomic weight 4404·64.

It forms with bases partly crystalline and partly amorphous compounds in definite proportions; the neutral salts contain 2 atoms of base; in many salts however only 1 atom of water is exchanged for a base; it has therefore a great tendency to form acid salts.

Anacardate of Potash.—The neutral salt is obtained by adding anacardic acid to a solution of caustic potash of moderate strength as long as it is dissolved without turbidness. No acid salt is eliminated by the addition of much water; but if a current of carbonic acid be passed into the concentrated solution, half the potash in the salt is converted into carbonate, and an acid salt falls in white flakes. To separate this from the carbonate of potash, the precipitate and liquid are evaporated to dryness over sulphuric acid, and the bianacardate of potash extracted with æther, which on evaporation left a white amorphous mass, readily soluble in alcohol and in pure water. The formula $2KO, C^{44} H^{30} O^5 + 2HO, C^{44} H^{30} O^5$ requires 12·06 per cent. potash; 14·22 were found. The excess is probably owing to the presence of some neutral salt.

Anacardate of Ammonia is prepared by dissolving the acid in ammonia. Dried *in vacuo*, the salt parts with ammonia, and forms a soapy amorphous mass, which yields a mucilaginous turbid liquid with water, but is again rendered clear by a few drops of ammonia. A small quantity of chloride of ammonium added to the solution separates the salt in a coagulated state.

Anacardate of Lime.—No precipitate is produced by an alcoholic solution of chloride of calcium in an alcoholic solution of anacardic acid. Ammonia produces a gelatinous, sometimes granular precipitate; the first dries to a brownish mass, which is difficult to powder. On calcination with sulphuric acid, after desiccation at 140° F., it gave 33·41 per cent. sulphate of lime, which corresponds to the formula

* C = 75·12, H = 12·48.

$2CaO, C^{44} H^{30} O^5 + 2HO$, which requires 33·38 per cent. sulphate of lime. The salt, dried at 212°, afforded 33·95 sulphate of lime; the formula $2CaO, C^{44} H^{30} O^5 + HO$ requires 34·13; but as the salt disengages the peculiar odour previously mentioned, it cannot be decided positively whether the salt loses 1 atom water.

Anacardate of Baryta, prepared by decomposing anacardate of ammonia with chloride of barium, forms a white precipitate, which becomes brown on drying. The salt, dried at 176°, afforded 47·6 per cent. sulphate of baryta; the formula $2BaO, C^{44} H^{30} O^5$ requires 47·82.

Anacardate of the Peroxide of Iron.—When alcoholic solutions of perchloride of iron and anacardic acid are mixed in the proportion to form $2Fe^2 O^3, 3C^{44} H^{30} O^5$, the gradual addition of ammonia does not throw down the whole of the anacardic acid in combination with iron, but a dark brown resinous deposit is formed, which is insoluble in water and in alcohol, but dissolves in æther, and on drying forms a hard mass, which is easily reduced to powder. Dried at 140° and ignited, it left 18·0 per cent. peroxide of iron, corresponding to the formula

$$Fe^2 O^3 HO, C^{44} H^{30} O^5 + 2HO = 2Fe^2 O^3, 3C^{44} H^{30} O^5 + Fe^2 O^3 3HO + 6HO,$$

which requires 18·47 per cent.

When the ammonia, instead of being added gradually to the mixture of anacardic acid and perchloride of iron, is poured into it at once in sufficient quantity to neutralize the acid, a reddish-brown precipitate is obtained, in which the 2 atoms of water of the crystallized acid appear to be replaced by 2 atoms of peroxide of iron; but on the addition of more ammonia than is requisite to neutralize the acid, the salt again loses a portion of the acid, and with a sufficient quantity of ammonia a salt was apparently formed, which contained double the amount of peroxide of iron. These compounds could however not be obtained pure, mixtures of the two being formed.

Anacardate of the Protoxide of Iron.—Protosulphate of iron produces in a solution of anacardate of ammonia a white precipitate, which darkens on exposure to the air.

Anacardates of Cobalt and Nickel.—The first forms a flocculent violet, the latter a white precipitate.

Anacardate of Lead is obtained as a heavy, granular, white precipitate when a boiling solution of anacardic acid is precipitated with an alcoholic solution of acetate of lead. It is also obtained on treating the following double salt with æther or boiling alcohol, but less crystalline. It afforded on analysis—

Carbon	47·23	47·68	44	= 47·43
Hydrogen	5·43	5·51	30	5·37
Oxygen	6·92	6·78	5	7·18
Oxide of lead....	40·42	40·03	2	40·02

The anacardate of lead soon becomes yellow and acquires a rancid odour.

Anacardate of Lead and Acetate of Lead.—I obtained this double salt during the cold season in the following manner:—The mixture of anacardic acid and cardol, as obtained by extraction of the shells with æther, was dissolved in a sufficient quantity of alcohol, and as much water added as possible without rendering the liquid turbid; it was then precipitated with an alcoholic solution of acetate of lead, which separated the greater portion of the acid with the colouring substance as a brown resinous mass. This consists principally of a double salt of anacardate with acetate of lead. To remove any adherent cardol, the brown mass is rinsed with alcohol, and then digested at a gentle heat with strong alcohol to which some acetic acid has been added. A turbid coloured solution is obtained, which is set aside in a moderately cold place until it has become clear and appears only slightly coloured. It is decanted from the sediment and exposed to a great degree of cold, when the salt separates in spherical groups, often of the size of a walnut, of radiating laminæ, which resemble cholesterine. They are perfectly white, and like talc to the touch, have a nacreous lustre, and are not altered at the ordinary temperature. The salt, dried at 122°, furnished on analysis the following results:—

	Found.	Calculated according to $PbO\overline{A}c + PbO, C^{44}H^{50}O^{5}, HO$.
Carbon	47·07	46·71
Hydrogen	5·55	5·50
Oxygen	10·94	11·66
Oxide of lead	36·35	36·13

It is consequently a combination of bianacardate of lead with the acetate, which is likewise confirmed by its behaviour towards sulphuric acid, various solvents, and at a high temperature. It is decomposed with evolution of acetic acid by sulphuric acid, is insoluble in cold alcohol, but on long-continued washing with it the crystals become dull upon the surface; and on boiling, the neutral salt separates, the acetic acid remains in solution and holds a little of the salt in solution. On treatment with æther, acetate of lead separates, and an acid salt is dissolved, which is left upon evaporation of the æther as an amorphous resinous mass, which is decomposed by alcohol into neutral salt and free acid. When the æthereal solution is set aside in a closed vessel, the latter salt likewise separates in minute warty masses and granules. This occurs immediately upon the addition of alcohol. It is insoluble in water, and when heated with it is converted into a white tenacious mass. When gently heated in a flask, it puffs up to a white frothy mass, giving off much acetic acid. On further application of heat, the frothy mass sinks to a colourless oily liquid, which at a higher temperature becomes brown and is decomposed.

Anacardate of Silver.—A neutral solution of silver produces in a concentrated solution of anacardic acid a heavy white pulverulent precipitate, which does not appear to be crystalline under the microscope. It dissolves in alcohol, especially in the presence of free acid, on which account no precipitate is produced in a dilute solution by

nitrate of silver. On the addition however of ammonia, a white flocculent precipitate separates. The first precipitate is very slightly and slowly altered by exposure to light, which is also the case with the latter except when a large excess of ammonia has been used, when during the drying it becomes brown, and after some time perfectly black, even in the dark. For analysis the salt was dried at 176°; at 267° it began to be decomposed, melting to a beautiful steel-blue mass. It contains in 100 parts—

Carbon	57·56	44	57·56
Hydrogen	6·82	31	6·74
Oxygen	10·25	6	10·45
Oxide of silver	25·37	1	25·25

The blackening of the salt precipitated by an excess of ammonia is occasioned by oxidation; for after drying at 176° the black salt afforded 56·35 C and 6·52 H, or one per cent. carbon and two-tenths per cent. hydrogen less than the formula AgO, HO, C^{44} H^{30} O^{5} requires.

I found it impossible to prepare the æther of anacardic acid.

Anacardic acid is readily dissolved in large quantity by *concentrated sulphuric acid*, and the solution exhibits a faint blood-red colour. It is reprecipitated by water, but in an altered condition; and when the sulphuric acid is allowed to become saturated with moisture by exposure to the air, a tenacious resinous mass is obtained, which readily dissolves in ammonia, and is again precipitated by acids in caseous flakes.

Nitric acid of 1·3 spec. grav. converts anacardic acid, at the ordinary temperature, after some time, into a porous light yellow body of extreme tenacity, so that it may be drawn out into long satiny threads. The nitric acid at the same time acquires a yellow colour. When heated there is a violent evolution of nitrous acid, and a yellow frothy mass is formed, which is gradually dissolved on boiling, while heavy oily drops subside, which are likewise dissolved by prolonged ebullition. When the syrupy residue is set aside for some time, it solidifies to a pasty mass of crystals. At a higher temperature the residue is carbonized, and oily drops sublime, which on cooling crystallize. The crystals appear to be suberic acid, but the small quantity obtained did not allow of further examination. The liquid which distilled over during the treatment with nitric acid was saturated with potash, evaporated to dryness, mixed with an excess of nitric acid, and again distilled, when some oily drops passed over, which possessed the characteristic odour of butyric acid. Anacardic acid affords therefore, on treatment with nitric acid, the same products as the other fatty acids; and in its combinations with bases a similar relation obtains as with stearic acid; both contain 2 atoms of water in their crystallized state, both or only one of which is exchanged for bases in their salts. But in its composition it approaches more closely to the resinous substances, a relation which is moreover supported by its occurrence in the free state; for in the balsam of anacardium it is neither combined with oxide of lipyle, nor is the

place of the latter assumed, as I first suspected, by the cardol. But it also resembles the oleic acid of linseed oil in composition; and that it becomes rancid in the air, like the other fats, is against its resinous nature, for no such change has hitherto been observed in the spontaneous decomposition of resins. Anacardic acid appears therefore to be most closely related to oleic acid.

[To be continued.]

On the Identity of Metacetonic and Butyro-acetic Acids.
By Messrs. Dumas, Malaguti and Leblanc.

Some years ago M. Gottlieb* obtained a new acid by oxidizing sugar with potash, which he called metacetonic acid, from its being likewise obtained from metacetone when submitted to the action of oxidizing agents. Subsequently M. Redtenbacher† found that glycerine furnished metacetonic acid under the influence of ferments; and at a later period he succeeded in separating considerable quantities from the product, which is obtained by oxidizing oleic acid with nitric acid.

We have found this same acid among the products resulting from the destruction of hydrocyanic æther by means of potash.

On the other hand, M. Nœllner had observed among the substances produced by the fermentation of the tartrate of lime a peculiar acid related to acetic acid, and to which on this account he gave the name of pseudo-acetic acid. This acid was subsequently carefully examined by M. Nickles‡, whose experiments showed that it possesses the same composition as metacetonic acid. From certain facts he was led to regard it as having a tendency to separate into butyric and acetic acids, whence the name butyro-acetic acid which he gave to it. M. Nickles insists upon certain facts, which in his opinion suffice to establish an essential difference between his acid and metacetonic acid; he points out several characters which separate them, but these characters evidently belong to the still imperfect history of metacetonic acid.

On comparing the acid extracted from the metacetonate of potash obtained from hydrocyanic æther, and the butyro-acetic acid derived from fermented tartrate of lime, we observed that these two acids were identical. They have the same composition which is expressed by the formula $C^6 H^6 O^4$, the same odour and the same appearance; they both crystallize at the ordinary temperature in plates analogous to those which acetic acid furnishes. They dissolve in water in every proportion, but float upon solutions of phosphoric acid and of chloride of calcium in the form of an oily stratum. They both boil at 286°. Their salts behave in the same manner when distilled with arsenious acid, disengaging products possessing the odour of alcarsine. The silver salts are identical in appearance and composition; the same applies to the baryta salts, both crystallizing in modified prisms belonging to the oblique rectangular system. All the angles

* Chem. Gaz., vol. iii. p. 157. † *Ib.*, vol. iv. p. 292. ‡ *Ib.*, vol. v. p. 58.

that could be measured are identical. From these facts we consider that we are entitled to conclude that the metacetonic, pseudo-acetic and butyro-acetic acids constitute but one and the same acid.

This acid deserves to be investigated with especial care; it is the first acid which exhibits the characters of a fat when ascending from formic and acetic acids to the fatty acids properly so called; it is the first which can be separated from its solution in the form of an oily layer; it is the first which furnishes with the alkalies salts which are unctuous to the touch like the alkaline soaps. These characters have led us to apply to it the name of *propionic acid*, which will call to mind its place in the series of the fatty acids, of which it is the first.

When one of us, five years ago, pointed out the existence of a group of acids possessing the general formula $C^n H^n O^4$, he was only able to enumerate eight acids which could be referred with certainty to this general formula, viz. formic, acetic, valerianic, œnanthylic, lauric, myristic, ethalic and margaric acids. To refer to this general formula butyric, caproic and capric acids, it was requisite to suppose a slight error in the interpretation of the analyses, otherwise so accurate, of M. Chevreul. Recent researches upon these three acids confirm this supposition most completely. But as there should exist between margaric and formic acids fifteen intermediate ones, six still remain to be discovered. These gaps have been almost entirely filled up by the metacetonic, caprylic, pelargonic, cocinic and benic acids, recently discovered by a more attentive study of the fatty bodies. At present we can therefore enumerate, by comprising anamyrtic acid, eighteen acids which form a continuous series. We may add, that some unpublished investigations of Mr. Brodie show that the general formula $C^n H^n O^4$, far from stopping at margaric acid, includes a new acid the composition of which is represented by $C^{54} H^{54} O^4$, or even acids with still higher formulæ. We are therefore already certain, limiting ourselves to the first of them, that there are eight fatty acids to be discovered between margaric acid and that the formula of which we have just given; and that these acids would be less fusible, more solid, and consequently better adapted, if they can be obtained to any extent, for certain purposes, for instance for giving light, than margaric acid. It is therefore of the highest interest to analyse with care the fatty substances of vegetable origin; in fact everything leads us to believe that these gaps will be filled up by them. However, we know so little of the fatty bodies which exist in insects, that no surprise should be occasioned if an attentive study of their materials should yield some of the terms which sooner or later will complete the series.—*Comptes Rendus*, Nov. 29, 1847.

On the Classification of the Silicates.

By Edward J. Chapman, Esq.*

The important natural class or family of the silicates is well known to comprise more individual species, in the usual acceptation of the

* Communicated by the Author.

term, than any other division of the mineral kingdom. An arrangement therefore of these bodies, based upon a system that shall exhibit the fundamental constitution of each in its relations towards the others, becomes, for the attainment of an onward progress in that branch of chemistry which has for its especial object the investigation of all natural inorganic bodies, not only a desideratum, but a necessity.

That such an arrangement has not hitherto been effected, few will disallow. That it is effected in the classification now proposed, I do not for a moment imply; but I make no apology in offering this classification to the notice of mineralogists, for the three following reasons, namely:—First, that it differs essentially from all that have preceded it; secondly, that it is founded, not only in its primary, but also in its secondary and subordinate divisions, upon a basis strictly chemical; and lastly, that I believe it to be a step in the right direction, and as such likely to tend and help, if but in a slight degree, towards the destruction of empirical classifications and the completion of a true system of mineralogy, the right path in the direction of which was first pointed out by the masterly conception of Berzelius in 1814*, although to meet for too long a time with neglect or opposition, owing to prejudice, to the desire of "having things simple and easy," and to the old mistaken notion, which even yet finds a few adherents, that mineralogy should be freed from the dominion of chemistry and become an exclusive science, an idea which no unprejudiced mind could for a moment maintain, and which happily is now, from its very weakness, nearly extinct.

I propose to divide the silicates into three principal groups,—1st, silicates of RO (protoxides); 2nd, silicates of R^2O^3 (sesquioxides, peroxides); and 3rd, silicates of RO in union with silicates of R^2O^3, with their subdivisions as in the following arrangement; in which, however, I have not attempted to give a list of all the silicates, as such would extend this paper beyond the limits allotted in a journal; but I have added only such examples of well-known or characteristic minerals as will serve to elucidate the subject, and render evident the merits or the demerits of my "distribution:"—

Silicates of RO.

1. *Anhydrous Silicates.—Ex.* Chrysolite (olivine) $3\left\{\begin{matrix}MgO\\FeO\end{matrix}\right\} + SiO^3$; gadolinite $3\left\{\begin{matrix}YO\\CeO\\FeO\end{matrix}\right\} + SiO^3$; willemite $3ZnO, SiO^3$†.

2. *Anhydrous Bi-silicates, per se, and with other Silicates.—Ex.* Wollastonite (table spar) $3CaO, 2SiO^3$; acmite $3\left\{\begin{matrix}NaO\\FeO\end{matrix}\right\} +$

* Essay on a purely Scientific System of Mineralogy, founded on the Electrochemical Theory and on the Doctrine of Chemical Proportions.

† The chondrodite might be arranged here, or otherwise amongst the fluorides. It is an olivine united to 1 atom of $MgFl^2$.

$2SiO^3$; the pyroxenes (augite, &c.) $3RO, 2SiO^3$; rhodonite (manganese spar) $3MnO, 2SiO^3$; the hornblendes $3RO, 2SiO^3 + RO, SiO^3$.

3. *Anhydrous Tri-silicates.—Ex.* Edelforsite CaO, SiO^3; talc MgO, SiO^3.

4. *Hydrous Sub-silicates.—Ex.* Sideroschisolite $6FeO, SiO^3 + 3H^2O$.

5. *Hydrous Silicates.—Ex.* Thorite $3ThO, SiO^3 + 3H^2O$; cerite $3CeO, SiO^3 + 3H^2O$; calamine (electric) $2(3ZnO, SiO^3) + 3H^2O$.

6. *Hydrous Bi-silicates.—Ex.* Dioptase $3CuO, 2SiO^3 + 3H^2O$.

7. *Hydrous Tri-silicates.—Ex.* Apophyllite $\left.\begin{matrix}KO\\CaO\end{matrix}\right\} SiO^3 + 2H^2O$?

8. *Hydrous or Hydrated Silicates of varying composition, the first series being perhaps isomorphous with Chrysolite, the second with Talc.—Ex.* (*a.*) Serpentine, schiller-spar, &c.; (*b.*) meerschaum, pimelite, &c.

SILICATES OF R^2O^3.

1. *Sub-silicates.—Ex.* Staurolite $2\left\{\begin{matrix}Al^2O^3\\Fe^2O^3\end{matrix}\right\} + SiO^3$; kyanite (disthene) $3\left\{\begin{matrix}Al^2O^3\\Fe^2O^3\end{matrix}\right\} + SiO^3$.

2. *Silicates.—Ex.* Bucholzite Al^2O^3, SiO^3; zircon Zr^2O^3, SiO^3; euclase $\left.\begin{matrix}Al^2O^3\\Gl^2O^3\end{matrix}\right\} SiO^3$.

3. *Sesqui-silicates.—Ex.* Bamlite $2Al^2O^3, 3SiO^3$.

4. *Bi-silicates.—Ex.* Phenakite $Gl^2O^3, 2SiO^3$; emerald $Gl^2O^3, 2SiO^3 + 2(Al^2O^3, 2SiO^3)$.

5. *Tri-silicates.*—No examples yet discovered.

6. *Hydrous Sub-silicates.—Ex.* Kollyrite $3Al^2O^3, SiO^3 + 15H^2O$; smelite (Glocker, Journ. für Prakt. Chem., xxxv. 39) $3Al^2O^3, 2SiO^3 + 6H^2O$.

7. *Hydrous Silicates.—Ex.* Malacon (Scheerer) $2(Zr^2O^3, SiO^3) + H^2O$; pholerite $Al^2O^3, SiO^3 + 2H^2O$.

8. *Hydrous Bi-silicates.—Ex.* Pinguite $\left.\begin{matrix}Fe^2O^3\\Al^2O^3\\3FeO\end{matrix}\right\} 2SiO^3 + 6H^2O$.

9. *Hydrous Tri-silicates.—Ex.* Anthosiderite $Fe^2O^3, 3SiO^3 + H^2O$; cimolite $Al^2O^3, 3SiO^3 + 3H^2O$.

SILICATES OF RO IN UNION WITH SILICATES OF R^2O^3.

A. *Anhydrous Silicates.*

1. *Silicates of* RO *with Sub-silicates of* R^2O^3.—*Ex.* Gehlenite $2(3CaO, SiO^3) + 2\left\{\begin{matrix}Fe^2O^3\\Al^2O^3\end{matrix}\right\}, SiO^3$.

2. *Silicates of* RO *with Silicates of* R^2O^3:—

(*a.*) *In the relation of* 3rSi *to* 2RSi.—*Ex.* Allanite $3(RO, SiO^3) + 2(R^2O^3, SiO^3)$; orthite?; lievrite (ilvaite) $3(3\left\{\begin{matrix}CaO\\FeO\end{matrix}\right\} SiO^3) + Fe^2O^3, SiO^3$.

(*b.*) *In the relation of* 1rSi *to* 1RSi.—*Ex.* Idocrase and garnets $3RO, SiO^3 + R^2O^3, SiO^3$; uniaxial mica $\left.\begin{matrix}KO\\3MgO\\FeO\end{matrix}\right\}, SiO^3 + \left\{\begin{matrix}Al^2O^3\\Fe^2O^3\end{matrix}\right\} SiO^3$ (H. Rose). Sodalite after Arfwedson's analysis might be placed here, or otherwise with the chlorides.

(*c.*) *In the relation of* 1rSi *to* 2RSi.—*Ex.* Epidote (zoisite) $3RO, SiO^3 + 2(R^2O^3, SiO^3)$; wernerite (scapolite) $3CaO, SiO^3 + 2(Al^2O^3, SiO^3)$. It is doubtful whether the nepheline do not belong to this section instead of to the following division.

(*d.*) *In the relation of* 1rSi *to* 3RSi.—*Ex.* Anorthite $3CaO, SiO^3 + 3(Al^2O^3, SiO^3)$ (Abich); amphodelite (Nordenskiold's) $3RO, SiO^3 + 3(Al^2O^3, SiO^3)$.

3. *Sesqui-silicates of* RO *with Silicates of* R^2O^3.—*Ex.* Iolite (dichroite) $2MgO, SiO^3 + 2(Al^2O^3, SiO^3)$ after a late analysis by Scheerer; nepheline $3\left\{\begin{matrix}NaO\\KO\end{matrix}\right\}, SiO^3 + 3(Al^2O^3, SiO^3)$. Bromeis gives the nepheline a formula analogous to that of the wernerite. The amphodelite, according to some analyses, should be transferred to this division.

4. *Bi-silicates of* RO *with Silicates of* R^2O^3.—*Ex.* Axinite $r\begin{matrix}Si^2\\B^2\end{matrix} + 2R\begin{matrix}Si\\B\end{matrix}$? The hauyne, after Rammelsberg's formula, might be arranged here, or otherwise with the sulphates.

5. *Bi-silicates of* RO *with Bi-silicates of* R^2O^3:—

(*a.*) *In the relation of* $1rSi^2$ *to* $2RSi^2$.—*Ex.* Weissite $3\left\{\begin{matrix}MgO\\KO\end{matrix}\right\}, 2SiO^3 + 2(Al^2O^3, 2SiO^3)$; glaucophane of Hausmann, a similar formula to that of the weissite, FeO, MgO, CaO and NaO, replacing MgO and KO.

(*b.*) *In the relation of* $1rSi^2$ *to* $6RSi^2$.—*Ex.* Leucite (amphigene) $3KO, 2SiO^3 + 3(Al^2O^3, 2SiO^3)$; andesin of Abich, an allied formula.

6. *Tri-silicates of* RO *with Silicates of* R^2O^3:—

(*a.*) *In the relation of* $1rSi^3$ *to* 1RSi.—*Ex.* Labradorite $\left.\begin{matrix}CaO\\NaO\end{matrix}\right\}SiO^3 + Al^2O^3, SiO^3$; pinite $\left.\begin{matrix}KO\\MgO\\FeO\end{matrix}\right\}SiO^3 + Al^2O^3, SiO^3$.

(*b.*) *In the relation of* $1rSi^3$ *to* 2RSi.—*Ex.* Couseranite?

(*c.*) *In the relation of* $1rSi^3$ *to* 3RSi.—*Ex.* Biaxial mica RO, $SiO^3 + 3(R^2O^3, SiO^3)$ Rammelsberg.

7. *Tri-silicates of* RO *with Bi-silicates of* R^2O^3.—(*a.*) *In the relation of* $1rSi^3$ *to* $1RSi^2$.—*Ex.* Oligoclase $NaO, SiO^3 + Al^2O^3, 2SiO^3$.

8. *Tri-silicates of* RO *with Tri-silicates of* R^2O^3.—(*a.*) *In the relation of* $1rSi^3$ *to* $1RSi^3$.—*Ex.* Felspar $KO, SiO^3 + Al^2O^3, 3SiO^3$; albite $NaO, SiO^3 + Al^2O^3, 3SiO^3$.

B. *Hydrous Silicates.*

9. *Silicates of* RO *with Silicates of* R^2O^3:—

(*a.*) *In the relation of* 1rSi *to* 2RSi.—*Ex.* Edingtonite?

(*b.*) *In the relation of* 1rSi *to* 3RSi.—*Ex.* Thomsonite $\left.\begin{matrix}CaO\\3NaO\\KO\end{matrix}\right\}SiO^3 + 3(Al^2O^3, SiO^3) + 7H^2O$ (Ramm.).

10. *Sesqui-silicates of* RO *with Silicates of* R^2O^3:—

(*a.*) *In the relation of* $1r^2Si^3$ *to* 1RSi.—*Ex.* Prehnite $2CaO, SiO^3 + Al^2O^3, SiO^3 + H^2O$.

(*b.*) *In the relation of* $1r^2Si^3$ *to* 2RSi.—*Ex.* Gismondine $2\left.\begin{matrix}CaO\\KO\end{matrix}\right\}, SiO^3 + 2(Al^2O^3, SiO^3) + 9H^2O$, after Marignac's late analysis.

11. *Bi-silicates of* RO *with Silicates of* R^2O^3:—

(*a.*) *In the relation of* $1rSi^2$ *to* 3RSi.—*Ex.* Brevicite $3\left.\begin{matrix}NaO\\CaO\end{matrix}\right\}, 2SiO^3 + 3(Al^2O^3, SiO^3) + 6H^2O$; fahlunite, an allied formula in which the RO = MgO, CaO, KO and MnO.

(*b.*) *In the relation of* $1rSi^2$ *to* 6RSi.—*Ex.* Rosite from Aker $3RO, 2SiO^3 + 6(Al^2O^3, SiO^3) + 6H^2O$.

12. *Bi-silicates of* RO *with Bi-silicates of* R^2O^3:—

(*a.*) *In the relation of* $1rSi^2$ *to* $3RSi^2$.—*Ex.* Analcime $3NaO, 2SiO^3 + 3(Al^2O^3, 2SiO^3) + 6H^2O$; chabasite $3RO, 2SiO^3 + 3(Al^2O^3, 2SiO^3) + 18H^2O$.

(*b.*) *In the relation of* $1rSi^2$ *to* $4RSi^2$.—*Ex.* Harmotome, $3BaO, 2SiO^3 + 4(Al^2O^3, 2SiO^3) + 18H^2O$; laumonite, an allied formula, 3CaO replacing the 3BaO of the harmotome.

13. *Tri-silicates of* RO *with Silicates of* R^2O^3:—

(*a.*) *In the relation of* $1rSi^3$ *to* 1RSi.—*Ex.* Mesotype (natrolite) $NaO, SiO^3 + Al^2O^3, SiO^3 + 3H^2O$; scolezite, a lime mesotype.

(*b.*) *In the relation of* $1rSi^3$ *to* $3RSi$.—*Ex.* Damourite (Delesse, Ann. de Chim. et de Phys., xv. 248) $KO, SiO^3 + 3(Al^2O^3, SiO^3) + 2H^2O$.

14. *Tri-silicates of* RO *with Tri-silicates of* R^2O^3:—
(*a.*) *In the relation of* $3rSi^3$ *to* $4RSi^3$.—*Ex.* Heulandite $3(CaO, SiO^3) + 4(Al^2O^3, 3SiO^3) + 18H^2O$.
(*b.*) *In the relation of* $1rSi^3$ *to* $3RSi^3$.—*Ex.* Stilbite $CaO, SiO^3 + 3(Al^2O^3, 3SiO^3) + 6H^2O$.

15. *Hydrous Silicates of* RO *with Silicates or Hydrates of* R^2O^3, *or Aluminates of* RO, *the composition of which is not yet thoroughly understood.*—*Ex.* Chloritoid, praseolite, pyrosclerite, chlorite, pennine, &c.

On the Action of Sulphuretted Hydrogen upon Hydramides.
By A. Cahours.

The experiments recently published by Liebig and Wöhler upon the products resulting from the action of sulphuretted hydrogen upon aldehyde-ammonia, induced the author to act upon the hydramides with sulphuretted hydrogen. A solution of hydrobenzamide in spirit is very soon rendered turbid when a current of sulphuretted hydrogen is passed through it, and with an excess of that gas, total decomposition occurs, in which no sulphur separates. When the final product is set aside for some time, a clear solution is obtained, which contains hydrosulphate of ammonia and an abundant deposit of a solid substance, which after washing with alcohol has the appearance of a perfectly white meal, and the composition and properties of the protosulphuret of hydrobenzoyle discovered by M. Laurent. The reaction between hydrobenzamide $= C^{42}H^{18}N^2$ and sulphuretted hydrogen giving rise to the formation of the protosulphuret of hydrobenzoyle $= C^{42}H^{18}S^6$ or $3(C^{14}H^6S^2)$, is exhibited by the following equation:—

$$C^{42}H^{18}N^2 + 10HS = C^{42}H^{18}S^6 + 4(HS, 2NH^3).$$

Cinnhydramide and anishydramide behave in the same manner; the products from both have considerable resemblance to that from hydrobenzamide. That from cinnhydramide has the composition $C^{18}H^8S^2$, and is called by the author *thiocinnole*. That from anishydramide is $C^{16}H^8S^2O^2$, and is called *thianisole*; the furfuramide of Fownes, $C^{30}H^{12}N^2O^6$, yields, on treatment with sulphuretted hydrogen, likewise a pulverulent substance of a yellow colour, the analysis of which led to the formula $C^{10}H^4S^2O^2$. This compound has received the name *thiofurfole*, from its composition resembling that of furfole $C^{10}H^4O^4$. An alcoholic solution of salhydramide is likewise converted by sulphuretted hydrogen into a pulverulent substance, very similar to the preceding, which colours persalts of iron violet-red, and combines with alkalies like the hydruret of salicyle, but contains a considerable amount of sulphur. The composition of this substance, found by analysis, agrees very well with that of a

hydruret of salicyle in which half the oxygen is replaced by sulphur $= C^{14} H^6 S^2 O^2$. It has already been shown by Laurent that his protosulphuret of hydrobenzoyle is formed by the action of sulphuret of ammonium upon oil of bitter almonds dissolved in alcohol; the author has ascertained that thiocinnole and thianisole are likewise formed when oil of cinnamon and the hydruret of anisyle dissolved in spirit are treated with sulphuret of ammonium. Oil of aniseed yields, by the same treatment, a resinous product containing sulphur, which is very difficult to obtain pure, and approaches by its composition sulphuretted cuminole, $C^{20} H^{12} S^2$. The aldehydes analogous to the oil of bitter almonds, which are enumerated in the first column of the following table, may be converted into their corresponding sulphur-compounds:—

$C^{14} H^6 O^2$	passes into	$C^{14} H^6 S^2$	= thiobenzole.
$C^{14} H^6 O^4$	...	$C^{14} H^6 S^2 O^2$	= thiosalicole.
$C^{18} H^8 O^2$	...	$C^{18} H^8 S^2$	= thiocinnole.
$C^{16} H^8 O^4$	...	$C^{16} H^8 S^2 O^2$	= thianisole.
$C^{20} H^{12} O^2$	...	$C^{20} H^{12} S^2$	= thiocumole.
$C^{10} H^4 O^4$	...	$C^{10} H^4 S^2 O^2$	= thiofurfole.

From this arrangement it will be seen, that by means of sulphuretted hydrogen that class of bodies to which Gerhardt has applied the name of hydramides, and by means of sulphuret of ammonium the oxygen compounds which they produce, may be converted into a series of sulphur compounds, the members of which differ by the entire or partial absence of their oxygen, and by the expelled atoms of oxygen being replaced by an equal number of atoms of sulphur.—*Comptes Rendus*, xxv. p. 457.

On some Properties of Carbon. *By* M. Lazowski.

The properties of carbon are numerous; they have been partly studied, but every day produces new facts: when it is in a state of ignition, it possesses some very remarkable properties.

When a piece of ignited charcoal, which is very clean and free from ash, is immersed in a solution of a metallic salt, it reduces the metallic salt which is contained in it, and the metal itself is deposited with all its natural brilliancy on the piece of charcoal. Thus the salts of tin, copper, platina, palladium, mercury, silver and gold, &c. furnish most brilliant deposits.

M. Lazowski has remarked, he says, that when the salts are too acid or too much concentrated, no effect is produced. The dilute solutions of the salts of copper often yield, by covering the charcoal, the most varied shades of colour, from the finest azure blue to that of metallic copper. The parts of the charcoal upon which certain metals are deposited in preference, are the extremities; whilst other metals cover equally all the surface of the reducing body; at other times, and this occurs with the protochloride of tin, the metal appears in very brilliant crystals, disseminated on the periphery of the charcoal.—*Journ. de Chim. Méd.*, Dec. 1847.

On the Equivalent of Selenium, with Observations on Selenious Acid. *By* F. Sacc.

Entertaining some doubts on the atomic weight of selenium, I obtained a quantity of this metalloid from Prague. To purify it from tellurium, sulphur and sulphate of lime, which it was found to contain, it was dissolved in nitric acid, evaporated, the residue sublimed, and thus separated from the tellurous acid and sulphate of lime. The acid, redissolved in water and filtered, was treated warm with bisulphite of ammonia to which hydrochloric acid was added, and the selenium thus obtained considered as pure; on re-solution in nitric acid, it left no residue on evaporation, and after neutralization, produced in solutions of salts of baryta, a precipitate soluble in dilute acids, and even in acetic acid, a sure proof of the absence of sulphuric acid. This experiment cannot be made with the sublimed selenious acid, because, as observed by M. Fisher, it always contains selenic acid, which forms with baryta a precipitate insoluble in acids.

Purified in this manner, the selenium became soft at 392° and melted at 482°; on cooling, it became viscous at 446°, at 392° ceased to adhere to the bulb of the thermometer, and became entirely solid at 302°; it may thence be concluded that its melting point is at 392°, and that of its solidification at 302°. However, as the latter cannot be fixed with certainty, on account of the selenium remaining for a long time viscous, it is probable that its point of solidification is situated very near 392°, its melting point. It is highly probable that its boiling point is somewhat higher than 1292°, the number generally admitted, as it cannot be distilled in retorts of French glass; it succeeds perfectly well in retorts of Bohemian glass.

To determine the equivalent of selenium, I adopted several methods in order to avoid as much as possible all chance of error, which is difficult on operating as is usually done upon one and the same compound. To obtain this end by checking as much as possible the results obtained, I converted the selenium into selenious acid; then the selenious acid, both free and combined with bases, into selenium; and also analysed several selenites. I first attempted, but without success, to oxidize the selenium by heating it in a current of dry air; but it does not take fire in it. In oxygen, on the contrary, it burns with a beautiful blue flame; but it is impossible to determine the composition of the selenious acid in this manner, because the current carries off a large quantity of vapours of unburnt selenium. With the hope of succeeding with condensed oxygen, I employed nitrous oxide, but with no success. Selenium may be sublimed in this gas, as in carbonic acid; so that this metalloid has less affinity for oxygen than nitrogen. This is likewise proved by the action of nitrate of ammonia, which on the application of heat reduces the seleuites, eliminating selenium. In this character selenium resembles the noble metals, to which it is also related by its ready precipitation by iron and zinc. However, this latter character is of less importance than the first, as it equally belongs to the two metals belonging to the arsenical group, as also to tellurium, which establishes the imperceptible transition of the oxygen group

to the arsenical group. Moreover, as the lower oxyacid of selenium is volatilized without decomposition by heat, while under the same conditions the higher oxyacid is decomposed, we cannot refuse to admit between the oxygen group and the preceding a most intimate connexion, such in fact that the illustrious Berzelius arranges, as is well known, selenium and tellurium among the electro-negative metals, at the head of which he places them immediately before arsenic and antimony, metals which approximate by many other characters to the two metalloids of the nitric group, phosphorus and nitrogen.

As I could not succeed in oxidizing selenium in a direct manner, I had recourse to nitric acid, which afforded the following composition for selenious acid :—

Selenium	70·99
Oxygen	29·01

I attempted, without success, to determine the amount of selenium converted into selenious acid in the form of selenite of baryta, after having carefully neutralized its solution in nitric acid or nitromuriatic acid with caustic soda or ammonia. In both cases, however large the excess of nitrate of baryta employed for precipitation, there remained in solution, even in the presence of a great excess of the alkali, so great an amount of selenious acid, that its estimation could not be accurate. It is probable that under these circumstances soluble double selenites are formed; this is especially the case in the presence of ammonia, as selenite of baryta may be dissolved in ammoniacal salts. It is likewise possible that certain polybasic alkaline selenites are not decomposed by barytic salts in the presence of water.

I next took perfectly dry selenious acid, and converted it into selenium by means of bisulphite of ammonia and hydrochloric acid, and obtained—

	I.	II.	III.	Mean.
Selenium	71·00	71·00	71·16	71·05
Oxygen	29·00	29·00	28·84	28·95

With these data we obtain the following equivalents for selenium :—

I.	II.	III.	Mean.
489·64	488·00	493·50	490·38

To check this equivalent, some selenite of baryta was heated with bisulphite of ammonia and hydrochloric acid, which thus yielded sulphate of baryta and selenium; the numbers furnished by experiment agreed closely with those obtained by calculation, adopting the equivalent 490·38 for selenium.

I. 0·8803 selenite of baryta gave of selenium and sulphate of baryta 1·0311; theory requires 1·0410.

II. 0·8172 selenite of baryta gave of selenium and sulphate of baryta 0·9497; theory requires 0·9663.

III. 2·9236 grms. selenite of baryta gave of selenium and sulphate of baryta 3·500; theory requires 3·4573.

The analysis of the residue II. having furnished 0·7180 sulphate of baryta, while the calculation indicates 0·7228, we may be assured

that the whole of the baryta existed in the state of sulphate in the mixture.

In the experiments I. and II. less substance was found than required by theory, from its being absolutely impossible to remove the whole of the precipitate from the vessels. But that the difference is owing to this mechanical cause is proved from the fact that it diminishes in proportion as the amount of selenite of baryta employed is increased.

I attempted to reduce a known weight of selenious acid by zinc without success from the very fine black powder which is precipitated retaining some zinc, which is only in part removed by boiling hydrochloric acid. Thrown into commercial nitric acid, it is instantly converted in the cold, with considerable disengagement of nitrous fumes, into selenious acid and oxide of zinc, which dissolve, while a white powder falls to the bottom of the vessel. If the liquid is precipitated with a large excess of carbonate of soda, the precipitate obtained, even on the employment of heat, contains a large quantity of selenious acid, so that it is impossible to analyse the selenite of zinc in this manner.

Wishing to confirm the equivalent found, I analysed several selenites. The first was the selenite of baryta, obtained by precipitating a neutral solution of nitrate of baryta by a neutral solution of selenite of soda. The salt, well washed, was dried at a red heat: care must be taken that it is entirely free from organic substances, the least trace of which occasions a partial reduction. The following are the results obtained:—

					Mean.
Selenious acid.....	41·97	41·93	41·93	41·96	41·95
Baryta.....	58·03	58·07	58·07	58·04	58·05

Whence it results that the equivalent of selenious acid is 691·49.

The selenites of silver and lead were then prepared by adding a solution of selenious acid to a neutral solution of nitrate of silver or nitrate of lead. The selenite of silver, on treatment with dilute hydrochloric acid, furnished too little chloride of silver, as it led to very variable numbers for the equivalent of the selenious acid, sometimes amounting even to 720. A still higher number was obtained on calcining a mixture of selenite of silver and concentrated hydrochloric acid. Pure concentrated sulphuric acid was then employed, which left a residue of sulphate of silver perfectly free from selenium, but constantly contaminated, however careful the calcination, by traces of metallic silver, which raised the equivalent of the selenious acid.

			Mean.
Selenious acid.....	32·42	32·25	32·335
Oxide of silver	67·58	67·75	67·665

leading to the equivalent 694·41 for selenious acid.

The selenite of lead was decomposed with an excess of sulphuric acid, and strongly calcined. The residue, heated with chloride of ammonium, gave with I. faint traces of selenium, larger amounts for II. and III. It was found impossible to remove the whole of the selenious acid from the selenite of lead by means of sulphuric acid,

a remarkable fact, as this acid entirely decomposes the selenite of baryta.

Selenious acid	32·97	32·37	30·26
Oxide of lead.....	67·03	67·63	69·74

leading to the equivalent 676·66 for selenious acid.

This equivalent is, like the preceding, too low, and not free from error; but the difference is not so serious as to induce us to entirely reject these analyses.

The selenite of soda was prepared by slightly supersaturating a tolerably concentrated solution of selenious acid with pure carbonate of soda. The liquid, evaporated to a syrupy consistence, was placed *in vacuo*, when it soon began to crystallize. Some beautiful crystals formed on the surface, which were carefully separated from the subjacent crystalline paste, and were dried in the water-bath at 194° until they no longer decreased in weight; they were then slightly effloresced, and had a faint rosy tint. They furnished—

	I.	II.	III.
Selenious acid volatilized on calcination	28·71	33·67	
Selenium in the residue	32·91 = SeO^2 46·31		
Selenium existing in the uncalcined salt	..	..	50·07 = SeO^2 70·47
Soda	..	28·22	

From these analytical data, and starting from the amount of soda furnished in II., which is very accurate, then raising to 71·78 the quantity of selenious acid contained in the salt, as the figure in III. is somewhat too low and the mean of I. and II. too high, the salt is approximately formed in 100 parts of—

Selenious acid.....	71·78
Soda	28·22

and we find that it is neither a neutral selenite nor a biselenite, but a chemical combination of 1 equiv. of each of these salts, which may be called a sesquiselenite, but which I regard as a biselenite of soda, having for base the neutral selenite of the same alkali. Calculated according to this formula, the centesimal composition of the salt becomes—

3 equivs. selenious acid	2072·79	72·61
2 equivs. soda	781·79	27·39
Equiv. of the salt.....	2854·58	100·00

We find in this a further proof of the possibility of the union of acid salts with neutral salts to form compounds, in which the first act the part of acids and the second that of bases, although both contain the same acid and the same oxide. I was led to adopt this formula from the loss which the salt experienced on calcination, which corresponds to nearly one-third of the selenious acid contained in the salt, while the other two-thirds occur, as required by the formula, in the residue in the form of neutral selenite.

Setting aside the results obtained by oxidizing selenium, as likewise those from the analyses of the selenites of lead and silver, although the error in the case of these latter is not in the same direction, the data furnished by the analyses of selenious acid, and those obtained by decomposing the selenite of baryta, will serve to fix the equivalent of selenium, as they are as free as possible from all sources of error.

The analysis of selenious acid affords—

For selenium.. 490·38; for seleniqus acid.. 690·38

The analysis of the baryta salt yields—

For selenium.. 491·49; for selenious acid.. 691·49

All attempts to prepare the oxide of selenium proved vain when the gas and the selenium were perfectly dry; but its odour instantly appeared when one or the other was moist; so that probably this gas is nothing else than air mixed with very minute traces of seleniuretted hydrogen.—*Ann. de Chim. et de Phys.*, xxi. p. 119.

Detection of Free Sulphuric Acid added to Wines.

The detection of a small proportion of sulphuric acid added to red wines, cannot be effected by means of barytic salts, for all wines contain greater or smaller quantities of the sulphates of potash and lime.

M. Lassaigne states that in an examination undertaken by him and MM. Ossian Henri and Bayard, they found that it was not possible to separate, by the action of pure sulphuric æther, four or five thousandths of sulphuric acid added to red wine, and consequently that this method did not always answer in proving the existence of this acid in the free state.

After many attempts, the authors ascertained a simple reaction, which allows of determining the presence of this acid, even when it exists in wines, in the proportion of a thousandth and a half.

When a piece of paper which has been touched with pure wine is dried at a gentle heat, the spotted portion is unaltered; whereas paper which has been moistened with wine, to which a very small quantity of sulphuric acid has been added, reddens, and becomes brittle and friable between the fingers when slightly rubbed, before the white paper becomes at all coloured.

Pure wine to which nothing has been added, leaves by spontaneous evaporation a violet-blue spot; whereas wine to which a very small quantity of sulphuric acid has been added (two to three thousandths), gives by drying a rose-coloured spot.

On examining into the sensibility of this simple process, the authors found that they were able to detect by its means one thousandth of sulphuric acid in red wine.

The paper most proper for the experiment is common glazed paper, containing starch or fecula. This kind of paper is well-known in commerce; and it is easy to discover it by the blue colour which it assumes when moistened with an aqueous solution of iodine.—*Ibid.*

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Researches upon Ox-Bile. *By* Dr. A. Strecker, *in a Letter from* M. Liebig *to* M. Pelouze.

I have induced Dr. Strecker, one of my assistants, to take up the investigation of ox-bile; and the results which he has obtained are highly interesting.

It appears from these researches that ox-bile consists principally of soda, potash and ammonia salts of two nitrogenous acids, only one of which contains sulphur. The nitrogenous acid free from sulphur is that discovered by L. Gmelin, and described under the name of *cholic acid.* It is prepared in the following manner:—The fresh bile is precipitated by neutral acetate of lead; the precipitate, washed and dried, is then exhausted with boiling alcohol of 0·848; a current of sulphuretted hydrogen is passed through this hot and concentrated solution to separate the lead; it is filtered, and the sulphuret of lead washed with a little water. This, when mixing with the alcoholic liquid holding the acid in solution, soon renders it milky; in this state it is set aside. In the course of twelve hours the whole liquid congeals to a crystalline mass, consisting of an infinite number of minute, silky, white needles; this is pure cholic acid. About 13·5 grms. of this acid is obtained according to this method from the bile of ten bladders, weighing in a dry state near 52 grms. 1000 parts of cold water dissolve 3·3 parts of cholic acid, and 1000 parts of boiling water 8·3 parts; from the hot saturated solution it crystallizes on cooling. It dissolves readily in alcohol, but cannot be obtained from it in crystals by cooling or by the evaporation of the solvent. The following formula expresses the composition of the crystallized acid, $C^{52}H^{43}NO^{12}$.

The metamorphoses which this acid experiences under the influence of alkalies and acids are most curious. When an aqueous solution of cholic acid is heated with an excess of baryta, it is gradually decomposed; after some hours' boiling it has disappeared, and its place taken by a new acid containing no nitrogen. Dr. Strecker has given this acid the name of *cholalic acid*; it is identical with the cholic acid of Demarçay. The formula $C^{48}H^{40}O^{10}$ expresses the composition of cholalic acid dried at 284°. In the crystalline state it contains 2 atoms of water.

It will be immediately perceived, that, on subtracting from the composition of cholic acid that of dried cholalic acid, we arrive at a formula which, with the addition of 2 atoms of water, exactly corresponds to the composition of glycocoll:—

Cholic acid	C^{52}	H^{43}	N	O^{12}
Cholalic acid	C^{48}	H^{40}		O^{10}
There remains	C^{4}	H^{3}	N	O^{2}
Plus 2 atoms of water		H^{2}		O^{2}
Crystallized glycocoll	C^{4}	H^{5}	N	O^{4}

Guided by these views, Dr. Strecker has succeeded, in fact, after removing the cholalic acid and the baryta, in obtaining from the residuary liquid beautiful crystals of glycocoll, the composition of which was proved by elementary analysis.

Cholic acid experiences an analogous decomposition by the action of strong acids. With hydrochloric acid hydrochlorate of glycocoll is obtained; but instead of the cholalic acid Demarçay's choloidic acid is formed; and if the action of hydrochloric acid is continued, the choloidic acid disappears, and Berzelius's dyslysine is obtained. The relation between these three compounds, cholalic acid, choloidic acid and dyslysine, is very simple; they differ from one another by a certain quantity of oxygen and hydrogen in the proportion to form water:—

Cholalic acid.....	C^{48}	H^{40}	O^{10}
Choloidic acid	C^{48}	H^{39}	O^{9}
Dyslysine	C^{48}	H^{36}	O^{6}

The decomposition of cholic acid by mineral acids is analogous therefore to that of hippuric acid, which, according to the beautiful discovery of M. Dessaignes, is decomposed under similar circumstances into glycocoll and benzoic acid.

The sulphuretted acid of ox-bile, when acted upon by acids, yields precisely in the same manner as cholic acid, choloidic acid and dyslysine; but, instead of glycocoll, *taurine*, which contains the whole of the sulphur of the bile. Dr. Bensch has determined the quantity of sulphur in the bile of different animals. He found—

In 100 parts bile of the calf	5·62	sulphur.
... ... sheep	6·46	...
... ... goat.....	5·55	...
... ... bear.....	6·38	...
... ... wolf.....	5·03	...
... ... fox	5·56	...
... ... chicken	5·57	...
... ... dog.....	6·21	...
... ... serpent	7·20	...

Ox-bile contains from 3·5 to 4 per cent. of sulphur. These numbers were obtained all from fresh bile, separated from fatty acids, and decolorized with animal charcoal. The quantity of sulphur refers solely to the organic substance or the purified bile, after deduction of the ash which it leaves on calcination.

As there exists in the living body, in the substance of the membranes and the gelatinous tissues, a body which, according to the beautiful researches of Braconnot, is decomposed by the action of acids and of alkalies into glycocoll and an acid free from nitrogen; since the cholic acid of the bile and hippuric acid behave precisely in the same manner, and since there is no other body in the animal organism which yields glycocoll by its decomposition, we may be allowed to suppose an intimate relation between these three substances. It is possible that the hippuric acid is a product of the metamorphosis of the gelatinous tissues, while the origin of the sulphuretted acid of the bile must be referred to the metamorphosis of the albuminous substances, which contain, as is well known, from $1\frac{1}{2}$ to 2 per cent. sulphur.—*Comptes Rendus*, Dec. 13, 1847.

Observations on Auriferous Glass. *By* Prof. H. Rose.

A few years ago M. Splittgerber* published some experiments on the remarkable property of white glass containing gold, of becoming of a beautiful ruby-red, when warmed or at an incipient faint red heat, without losing its transparency. He found that this took place in oxygen gas and in hydrogen gas, and even in closed crucibles filled with sand, powdered charcoal, or peroxide of tin. I have recently made some experiments upon a colourless gold glass, which had been prepared in Silesia. I found that it became ruby-red both when heated in an atmosphere of oxygen and in one of carbonic acid; but when heated to redness in hydrogen, it became but slightly reddish and coloured gray, evidently from the oxide of lead contained in it being reduced. When the glass was exposed to a higher temperature, at which it began to become somewhat soft, these places acquired a liver-colour. In the flame of the oxyhydrogen blowpipe the red glass fused to colourless drops; but I could not succeed in restoring the ruby-red colour to this colourless glass by heating it as stated by Splittgerber.

M. Splittgerber is of opinion that the colourless gold glass contains a silicate of the peroxide of gold, which is converted by heat into protoxide, the intense colouring power of which produces, when present even in minute quantity, a dark colour in the glass; but as we are not able to combine peroxide of gold with acids either in the moist, and still less in the dry way, and properly speaking we are not acquainted with a single saline compound of it, the existence of a silicate of the peroxide of gold is not very probable; but even should such exist in the colourless gold glass, there appears to be no reason why it should lose oxygen at a far lower temperature than requisite for its production, becoming converted into protoxide even in an atmosphere of oxygen.

Now, on the other hand, we know that the protoxide of gold, as a base, is far more stable in its compounds than the peroxide. We know that the purple of Cassius, which, according to the recent views of Berzelius, is a double compound of the proto-

* See Chem. Gaz., vol. iii. p. 340.

stannate of tin and protostannate of gold, can bear a high temperature without decomposition; it appears therefore to me to be far more in accordance with nature to admit a protosilicate of gold in the colourless glass, which, like the purple of Cassius, can, in combination with other silicates, support a high temperature without decomposition. When a neutral salt of this kind, or perhaps an acid colourless silicate, is heated again, and at a lower temperature than that at which it had been produced, a portion of the protoxide of gold separates. It is this eliminated protoxide of gold which is capable of colouring an immense quantity of flint glass. This view appears to be supported by several analogies which the gold glass exhibits with glass containing protoxide of copper. The protoxides of gold and copper have not only the same atomic composition, but likewise resemble each other very much in their properties.

In some glass-houses a glass is made with protoxide of copper, of a similar ruby-red colour to that possessed by the heated gold glass; like that it is colourless after fusing, and also acquires the red colour when warmed. Now this is effected not by a reduction of any peroxide of copper to protoxide, for the colourless glass becomes red when heated even though coated on both sides with white flint-glass. The colourless glass, moreover, acquires a green colour when heated for some time in an atmosphere of oxygen, which is owing to peroxide of copper; in carbonic acid, on the contrary, it becomes red. In a current of hydrogen the copper in the glass is reduced; but at the same time the oxide of lead which is contained in it in far greater quantity. We see therefore that the silicate of the protoxide of copper is colourless, and may be rendered red at a lower temperature than that at which it was formed. This becoming red evidently arises from a portion of the protoxide of copper being eliminated by the heat; and although but a mere trace is set free, it is able, from its intense colouring power, to impart a deep colour to a large quantity of glass.

Every chemist acquainted with the use of the blowpipe is aware that similar phænomena are exhibited when a minute quantity of peroxide of copper is dissolved either in borax or in microcosmic salt and the beads are exposed to the reduction-flame. Both the glasses are perfectly colourless when the oxide of copper has been reduced in the inner flame to protoxide, and become red on cooling, generally on solidification. With a very minute trace of copper, the colourless bead of microcosmic salt frequently remains of a transparent ruby-red colour on solidification.

The expression introduced into science by Berzelius, of "flaming" a glass opake, refers to all those numerous cases where the beads are exposed for a long time to a temperature not quite sufficient to fuse them. Under such circumstances borax beads form an enamel when the boracic acid has been saturated to a certain degree with oxide. The circumstance that the gold or protoxide of copper glass which has become red has not lost its transparency, is not opposed to the supposition that the colouring is owing to the elimination of the metallic protoxides, as extremely minute traces of opake sub-

stances impart a colour even to aqueous solutions without lessening their transparency; thus, for instance, very small quantities of sulphuret of lead or sulphuret of iron impart a brown or green colour to liquids without rendering them opake.

Gold glass, which has become red by heating, turns brown at a higher temperature. This is owing to the eliminated protoxide of gold being reduced to metal, while that which is in combination with silicic acid withstands even the fusing heat of the glass.—*Bericht der Berlin. Acad.*, Oct. 25, 1847.

Researches on Santonine. *By* W. Heldt.

Santonine was discovered and described by Kahler and Alms, and subsequently carefully investigated by Oberdörffer, and especially by Trommsdorf. In the following communication the author gives further data, and especially analytical, respecting santonine, to which Calloud and Mialhe have recently ascribed the well-known vermifuge properties of the extract of worm-seed. According to the author, santonine crystallizes very readily from its solution in spirit in nacreous prisms, which do not effloresce.

The following analyses were made with substances prepared at different times:—I. crystallized from alcohol, and dried over sulphuric acid; II. fused; III. crystallized from æther, and dried at 212°; IV. crystallized from boiling water, and dried in the air:—

	I.	II.	III.	IV.			
Carbon....	73·70	73·30	73·24	73·01	5=379·27		73·41
Hydrogen	7·29	7·37	7·38	7·48	3	37·43	7·24
Oxygen ..	19·01	19·33	19·48	19·51	1	100·00	19·35

These analyses agree with those made by Liebig and Ettling, who employed fused santonine. When boiled with large quantities of a dilute solution of caustic potash, santonine dissolves without subsequently separating. Strong acids precipitate it from such a solution immediately, acetic acid only after some time; but in both cases the substance is obtained unaltered. Under certain circumstances santonine exhibits after fusion, especially that separated by acetic acid from the solution in potash and that cooled rapidly after fusion, the peculiar property of frequently not solidifying, but forming a tenacious gummy mass, but which may be restored to the crystalline state by the vapour of æther or alcohol at the ordinary temperature, or by moistening it with a few drops of these liquids. It is merely necessary to hold a watch-glass containing some amorphous santonine with its concave surface over a vessel containing alcohol or æther, to cause the tenacious mass to solidify. At first some granules are formed in it, around which prismatic crystals arrange themselves concentrically, and then extend throughout the mass. When the amorphous santonine is exposed to a temperature of 104°–122°, it likewise reacquires its crystalline condition. As already observed by Trommsdorf, the light of the sun exerts a very peculiar action upon crystals of santonine. Ten minutes after the action they become yellowish, and then gradually of a darker yellow, decrepitating violently, upon

which they assume a golden colour. This yellow santonine behaves, as was likewise observed by Trommsdorf, in a different manner towards potash and alcohol from the white; it affords a yellow solution, whilst the white dissolves with a carmine colour. When the yellow amorphous pieces of santonine are dissolved in alcohol, and the solution, protected from the light, left to spontaneous evaporation, white rhombic tablets are obtained, which however dissolve with a yellow colour in an alcoholic solution of potash, and again become yellow in sunlight. The yellow body melts when heated to a yellowish liquid, and solidifies on cooling. It does not differ from white santonine in composition, for when dried at 212° it afforded 73·20 carbon, 7·31 hydrogen, and 19·49 oxygen. But this yellow santonine can easily be converted into the white; when dissolved in potash and separated from this solution with muriatic acid, it has all the properties of the original white santonine, and dissolves no longer with a yellow colour, but like that with a carmine colour, in an alcoholic solution of potash.

Combinations of Santonine with Bases.—The soluble combinations of this class are obtained by digesting the alcoholic solution of santonine with oxides or carbonates; the sparingly soluble by precipitating their salts with santonine-potash, or the corresponding soda compound. The affinity of santonine for the metallic oxides is so slight that these combinations are decomposed by mere boiling. When the metallic oxides are digested with alcohol and santonine, the liquid assumes a beautiful carmine colour, which subsequently disappears. This colour is not formed without the presence of alcohol. When santonine is melted with the oxides, red combinations are likewise formed if the bases are not very weak. If water is added to santonine-potash or soda prepared in this manner, the compound subsequently acquires a perfectly white colour, which is probably owing to water separating from the santonine on its combination with bases, and the anhydrous substance yielding red compounds, which subsequently become colourless by the reabsorption of water. The compounds of santonine with the alkalies and the alkaline earths dissolve most readily both in water and in alcohol; they are not altered by carbonic acid nor by exposure to sunlight.

Santonine-Soda, $C^{30}\,H^{18}\,O^{6}$, NaO HO + 7HO, and at 212° $C^{30}\,H^{18}\,O^{6}$, NaO HO.—This compound is obtained by digesting dry carbonate of soda with an alcoholic solution of santonine. The liquid, which is at first of a carmine colour, and subsequently becomes colourless, is evaporated to dryness at a temperature of 86° and the residue exhausted with absolute alcohol, which removes the santonine compound. If an excess of carbonate of soda has been employed, the whole of the santonine is held combined with soda; no carbonic acid is set free in the formation of this compound, but a bicarbonate is produced. Santonine-soda forms a tissue of minute needles, which are not altered by exposure to the air or by sunlight; they have a strong alkaline taste and reaction. Mineral acids eliminate santonine immediately, acetic acid after a long time, in crystals. Larger crystals are obtained by dissolving the latter in

as little water as possible, and leaving the solution to spontaneous evaporation. The air-dried salt lost at 212°, after fusing in its water of crystallization, 17·5 per cent. of water, and left after ignition a quantity of carbonate of soda corresponding to 8·75 per cent. soda. The above formula requires 17·9 water and 8·9 soda. The salt dried at 212° moreover contained 10·4 per cent. soda, which likewise agrees with the amount required by the second formula, which is 10·8. At a higher temperature the last atom of water escapes, and the salt acquires a carmine colour, but in contact with the moist atmosphere reacquires this water and again becomes colourless.

Santonine-Potash and Santonine-Ammonia.—The first is prepared like the preceding salt; it forms a gummy amorphous mass. When an alcoholic solution of santonine is added to an alcoholic solution of santonine-potash, and the whole evaporated, the free santonine first separates in a crystalline state, and subsequently the potash compound amorphous. Santonine could not be combined with ammonia either in the moist or dry way.

Santonine and Lime, $C^{30}H^{18}O^6 CaO + HO$ (at 212°).—An alcoholic solution of santonine is digested with hydrate of lime until the carmine colour disappears; the solution is then filtered and evaporated at a constant temperature of 86°. Water dissolves the lime compound from the dry residue, leaving behind some carbonate of lime, and yields on evaporation at 86° crystalline crusts, which separate on the surface and are removed. After washing with water and drying, they form a silky mass, which is not altered by the air, sunlight or carbonic acid. It has an alkaline taste. Chloride of calcium, mixed with santonine-potash, affords a white precipitate of santonine-lime. On analysis of the salt dried at 212°, it was found to contain 10·4 per cent. lime; the above formula requires 10·00.

Santonine and Baryta, $C^{30}H^{18}O^6$, $BaO + 2HO$ (at 212°).—This compound was prepared exactly in the same manner as the lime salt. It behaves similarly, and affords, on the evaporation of the aqueous solution, a gelatinous crust, which forms when dried a loose white powder. All the compounds above enumerated afford on destructive distillation as chief product a yellow oily substance, which on cooling solidifies, and dissolves in an alcoholic solution of potash with a carmine colour. It is perhaps identical with the red substance into which santonine is converted at a high temperature.

Santonine and Oxide of Lead, probably $C^{30}H^{18}O^6$, $PbO + HO$ in the dry state.—On mixing a boiling alcoholic solution of santonine with an aqueous solution of acetate of lead, and evaporating at between 86° and 104°, preventing the carbonic acid of the atmosphere having access to it, warty groups of crystals, composed of minute pearly needles, separate, which are long washed with water to remove the basic acetate of lead which tenaciously adheres to them. A certain amount of the compound dissolves on washing it with water. The salt obtained in this manner left 33·60 and 33·82 per cent. oxide of lead, numbers which lead not to the above formula, but to $5(C^5H^3O)$. The salt was consequently prepared in a different manner, by precipitating a solution of acetate of lead with santonine.

The white precipitate, after washing with water, was dried at 212°, in which state it afforded 31·18 per cent. oxide of lead; the formula $C^{30}H^{18}O^{6}PbO$ requires 31·18; however, the result must only be considered as an approximative one.

Santonine-potash produces sparingly soluble white precipitates in concentrated solutions of sulphate of zinc, nitrate of silver, proto- and persalts of mercury; and in salts of iron, a cream-coloured, in copper a blue, in oxide of uranium salts a yellow, and in salts of oxide of chromium a green precipitate. All the sparingly soluble precipitates are decomposed into their constituents when boiled with water or alcohol.

Products of Decomposition of Santonine.—When chlorine is passed into water containing santonine in suspension, it acts but imperfectly upon it; on the contrary a yellowish-red substance is obtained after treating the hot alcoholic solution with chlorine, which remains, after evaporating the alcohol, as a resinous mass. A brown resin is formed with evolution of muriatic acid by the action of chlorine gas upon melted santonine. A crystalline chlorine compound is obtained when santonine is dissolved in muriatic acid and some alcohol, and then poured in small portions into chlorate of potash, and dissolving the white amorphous mass which separates on the surface after sufficient washing with water, in absolute alcohol. The compound separates in crystals on the spontaneous evaporation of the solution. When the operation has been well performed, the crystals are obtained perfectly white; after the first crystallization they contain no unaltered santonine, which would have easily been detected by its change of colour on exposure to the light. They dissolve in æther and alcohol, but not in water; an addition of the latter renders the alcoholic solution milky, upon which the substance is deposited in a crystalline state. The crystals themselves are tasteless; they grate between the teeth; their solution in alcohol is excessively bitter to the taste. They afford at a high temperatnre a yellowish oil, which, like melted santonine, becomes solid on cooling. Ammonia does not alter the crystals when the chlorinated substance is exposed for several weeks under a bell-glass to an atmosphere of ammoniacal gas, or when ammonia is added to a saturated alcoholic solution of it. By digestion with potash and alcohol, an orange-coloured solution is formed, from which, on further concentration, orange drops of a potash compound separate, which on continued evaporation appear indigo-blue. If the potash is removed by sulphuric acid, and the excess of this by carbonate of baryta, a red liquid is obtained, which on evaporation to dryness and exhaustion with absolute alcohol, leaves a red resin on evaporation. The crystals gradually assume, in the direct light of the sun, a red, and finally a dark brown colour, without changing their form, owing to the production of a brown resin upon their surface, with elimination of muriatic acid; this coating can be removed by digestion with alcohol from the unaltered inner nucleus. This change likewise occurs in hydrogen, and is consequently not owing to the oxygen of the atmosphere. The substance, dried at 212°, afforded on analysis—

Carbon	57·6	57·4	..	30 =	2274	57·45
Hydrogen ..	5·3	5·4	..	16	200	5·05
Chlorine....	..	..	21·8	2	884	22·33
Oxygen	..	..	..	6	600	15·17

According to this analysis the relation between the chlorinated santonine and santonine is expressed in the following formulæ:— $C^{30}H^{16}O^{6} + Cl^{2}$ and $C^{30}H^{16}O^{6} + H^{2}$.

Iodine has no action upon an alcoholic solution of santonine. When melted with iodine, it is decomposed. *Bromine* instantly decomposes santonine, with evolution of bromide of hydrogen. When the santonine is mixed with water or dissolved in alcohol before adding the bromine to it, it is converted into a brown resin, which is soluble in alcohol and æther. When bromine is added in drops to a very dilute solution of santonine, a compound perfectly similar to the preceding chlorinated body is formed, which separates on spontaneous evaporation. When dry it acquires a bright yellow colour in sunlight, and gradually a dark purple-red one when moist even in the dark. It is decomposed at 212°. Phosphorus, ignited by the temperature of the melting santonine, converts it into a dark brown resin.

Action of Acids upon Santonine.—Acetic and concentrated muriatic acids dissolve santonine unaltered. After long digestion with concentrated muriatic acid, it is partly decomposed; yellow oily drops of a resinous substance separate, which on cooling become solid. Santonine dissolves in moderately dilute sulphuric acid with the application of heat, and again separates unaltered on cooling. Concentrated sulphuric acid dissolves santonine to a yellow liquid, which subsequently becomes red, being decomposed. On long digestion with dilute sulphuric acid a yellow oily substance is formed, as with muriatic acid. Dilute, concentrated, and even fuming nitric acid, dissolve santonine on the application of heat, but on cooling it again separates unaltered. After long digestion with nitric acid, a viscous, amorphous, bitter mass, containing no nitrogen, is first produced; on further continued oxidation, and after expelling the acid, a gummy, extremely bitter substance is formed, which dissolves in water and in alcohol. The final product of oxidation is an acid, which crystallizes in needles, and which reacts like succinic acid. The liquids which distil over in the treatment with nitric acid contain prussic acid. Chromic acid, employed in the form of a solution of bichromate of potash and sulphuric acid, acts but imperfectly on santonine, owing to its sparing solubility. When a solution of santonine in concentrated sulphuric acid is mixed with bichromate of potash, or santonine with chromic acid, it is immediately decomposed. When santonine is heated to boiling upon a stratum of fused phosphoric acid, a yellow liquid is obtained, which on cooling forms a yellowish-brown resin soluble in alcohol. Phosphoric acid gives rise to the production of a similar substance in an alcoholic solution of santonine.

When peroxide of lead is mixed with santonine and heated to the fusing-point of the latter, the fused mass takes fire. If the heating

is immediately discontinued, acrid yellow vapours are given off, which condense to a solid substance in reticulate figures upon the cold sides of the vessel, and which dissolve with a red colour in hot alcohol. This alcoholic solution contained a brown resin and unaltered santonine. Permanganate of potash and a mixture of permanganate of potash with nitric acid do not alter santonine even when the latter is held in solution by alcohol.

Santonine is not a true acid, but a crystalline resin. Most of its products of decomposition are resinous substances, and the final product of oxidation by nitric acid is succinic acid, which is formed under similar circumstances from resins and fats. It has the same centesimal composition as anhydrous caryophyllic acid, eugenine, crystallized cuminic acid, and the Alpha resin of benzoin.—Liebig's *Annalen*, vol. lxiii. p. 10.

On the Peculiar Constituents of the Fruit of Anacardium. *By* Dr. Stædeler.

[Continued from p. 36.]

Cardol.—The liquid from which the anacardic acid has been removed by hydrated oxide of lead contains the cardol mixed with some of its products of oxidation in combination with ammonia. To separate the latter, the liquid is boiled with small quantities of hydrated oxide of lead, when ammonia is evolved, and a violet lead compound subsides; the filtered solution affords, after distilling off the alcohol, cardol of a dark vinous-red colour. For further purification, the concentrated solution is mixed with water until the appearance of a slight opacity, an aqueous solution of acetate of lead added, heated to boiling, and basic acetate of lead added in drops until the liquid has nearly lost all colour, and a brown sediment is formed, which adheres firmly to the glass. If the solution be mixed only with sesquibasic oxide of lead, it frequently becomes perfectly colourless, and a violet pulverulent precipitate is formed; but the precipitate consists for the greater part of a cardol compound, so that a great loss of cardol is occasioned. The excess of lead is removed from the decolorized solution by sulphuric acid, and the cardol obtained by distilling off part of the alcohol and mixing with water.

In small quantities it forms a yellow oily liquid, but in larger quantities it always exhibits a reddish colour, although it would appear to be perfectly colourless in the pure state. It is however so readily oxidized in the presence of basic lead salts, that the colourless solution during filtration becomes faintly flesh-coloured, and after a time deposits a violet precipitate. When purified from foreign ingredients, it alters very slowly; and even on exposure to the air it is a long time before it becomes darker. It is insoluble in water, but readily soluble in alcohol and æther, and the solutions do not alter coloured test-papers. It has no smell in the cold, but when warmed diffuses a faint agreeable odour. Its specific gravity is 0·978 at 74° F.

It is not volatile, but is decomposed at a high temperature into a very mobile liquid. It burns with a very smoky luminous flame.

The analyses were made with cardol prepared at different times and dried at 212°, and afforded the following results:—

Carbon	80·00	80·08	42 =	80·04
Hydrogen	9·86	9·80	31	9·81
Oxygen	10·14	10·12	4	10·15

Atomic weight = 3941·92. No nitrogen, sulphur or phosphorus was found in it.

Cardol combines with bases, but its affinity is very slight, and the combinations with those oxides which readily part with their oxygen are reduced.

A solution of neutral acetate of lead produces no precipitate in solutions of cardol; basic salts of lead a white one, which dissolves easily in alcohol, and soon becomes flesh-red, and subsequently reddish-brown in contact with the atmosphere in a moist state. The solvent must therefore be weak spirit from which the air has been removed by boiling, and the precipitate washed and dried *in vacuo*. It afforded on analysis—

		Calculated according to the formula $PbO\,\overline{Ac} + 3PbO, C^{42}H^{31}O^{4}$.
Carbon	34·25	34·02
Hydrogen	4·20	4·18
Oxygen	6·74	6·88
Oxide of lead	54·81	54·92

The precipitate is consequently a combination of acetate with cardol-oxide of lead, and the cardol enters into the combination without loss of water. This view is confirmed from the fact, that on adding sulphuric acid to the salt acetic acid is eliminated; and on washing the precipitate with water instead of weak spirit, lead is removed; and on burning the precipitate, it was found to contain only 40·71 per cent. oxide of lead; so that it would seem that the acetate of lead exists in the compound, not as neutral but as basic salt.

On mixing a solution of cardol with nitrate of silver, no reaction takes place; and on evaporating the alcohol unaltered cardol separates. On the addition of ammonia a bright-coloured flocculent precipitate subsides, which is decomposed immediately after its production, the sides of the vessel becoming coated with a film of metallic silver.

Concentrated Sulphuric Acid dissolves cardol easily, and with an intense red colour; and if the sulphuric acid is allowed to become saturated with moisture by exposure to the air, brownish-yellow crusts separate, which are easily reduced to powder, and are nearly insoluble in water. If sufficient water is added at once, taking care to cool the mixture well, a slightly-coloured gummy mass separates, which is soluble in water. The solution, boiled with carbonate of barytes, contains but traces of an organic substance. Alcohol containing sulphuric acid extracts from the baryta compound a substance which, on evaporation of the solvent, separates in resinous masses, and may easily be reduced after drying to a slightly-coloured powder. No compound sulphuric acid is formed.

The action of *nitric acid* upon cardol varies with the temperature and degree of concentration. Moderately dilute nitric acid converts it after some time into a thick brilliant carmine-coloured substance, which is insoluble in aqueous solutions of caustic potash and ammonia, but dissolves on the addition of alcohol, and affords with acetate of lead a violet flocculent precipitate, which appears to be identical with that formed by the action of caustic potash subsequently described.

When cardol is added by degrees to an acid of 1·3 spec. grav., cautiously avoiding a rise of temperature, a gentle but constant evolution of gas results, and a brick-red mass is formed, which subsequently changes into a lively vermilion-red powder. It is very sparingly or not at all soluble in alcohol: water constantly removes something from it, and it becomes yellow; but it could not be obtained free from nitric acid by long-continued washing. When the mixture of cardol and nitric acid is heated, a violent disengagement of nitrous acid results, and an orange-coloured porous resin is formed, which after long boiling is dissolved by the nitric acid with a yellow colour. The solution has a very bitter taste, deposits a yellow soft resin on the addition of water, and affords a yellow precipitate with acetate of lead, which burns with a slight explosion. When the solution is evaporated to dryness, and the residue heated more strongly, suberic acid appears to sublime, and volatile fatty acids could be detected in the liquid which distilled over. It was not ascertained whether the latter products resulted from a slight admixture of anacardic acid, but the cardol employed was not perfectly pure.

When a moderately strong *solution of potash* is poured upon cardol, it is immediately converted into a yellowish tenacious mass, which after some time dissolves. With access of air the solution acquires an intense blood-red colour, and yields with most of the earthy and metallic salts red or violet precipitates. The red mass was exposed to an atmosphere of carbonic acid, then evaporated as much as possible and digested with alcohol, which removed a brilliant red potash salt, leaving a residue of carbonate of potash. The boiling solution was mixed with an alcoholic solution of acetate of lead, when some carbonate of lead fell. The filtered liquid afforded, on the addition of a few drops of ammonia, a violet precipitate, which dissolved in alcohol with an intense red colour, and was again precipitated with a little ammonia. It afforded on analysis 62·8 per cent. oxide of lead, 27·5 carbon, 3·2 hydrogen, and 6·5 oxygen. This corresponds to a combination of cardol with 5 atoms of oxide of lead, in which the former has parted with 1 atom of water and absorbed 5 atoms of oxygen.

When the solution of cardol in potash is exposed for some time to the air, and at the same time kept at a temperature of 140° to 176°, the mixture assumes a brownish-red colour. The free potash still contained in it was saturated with carbonic acid, when a brown resinous compound separated in tolerably firm masses, which were readily purified by washing with water from adherent carbonate of

potash. The compound was dissolved in æther, this for the greater part evaporated, and the residue treated with alcohol, which dissolved a great portion, leaving behind a blackish-brown potash compound, of which more was deposited on the expulsion of the last traces of æther. The alcoholic solution is dark reddish-brown by transmitted light, and of a beautiful green and perfectly opake by reflected light. This remarkable dichroism is not destroyed by an addition of potash, but acids turn the solution dark yellow.

Acetate of lead produced a reddish-brown precipitate, which upon drying became cinnamon-brown, and readily subsided from the light yellow liquid, which afforded a white precipitate with basic salts of lead, and appeared to contain some undecomposed cardol. The precipitate by neutral acetate of lead was insoluble in alcohol, but dissolved in æther, and was again separated from this solution by the addition of alcohol. After being dried at 176°, it was analysed, and afforded—

Carbon	50·96	84 =	49·91
Hydrogen	6·05	60	5·92
Oxygen	11·47	14	11·08
Oxide of lead	32·08	3	33·09

leading to the formula $3PbO + 2C^{42} H^{30} O^{7}$. From want of material it was impossible to subject the substance combined with the oxide of lead to analysis; but it is probable that in the free state it contains 1 atom of basic water, and its formation is then readily explained by supposing the cardol under the influence of alkalies to combine with as much more oxygen as it already possessed:—

$$C^{42} H^{31} O^{4} + O^{4} = C^{42} H^{30} O^{7} + HO.$$

When cardol is mixed with hydrated oxide of lead, and the mixture exposed for some time to the atmosphere, moistening it now and then with alcohol, the mixture soon acquires a violet colour, and the same bodies appear to be formed as above described in their lead compounds; for boiling alcohol removes a red lead compound from it, leaving the greater part behind of a brownish-red colour.

The latter products of decomposition are interesting, as they are the cause of the red colour of the mixture of cardol and anacardic acid; they are contained in this mixture in the form of ammoniacal compounds, and appear to be formed gradually, as sound healthy fruit yield a light-coloured ætherial extract, while old and injured fruit yield a very dark-coloured solution. The source of the ammonia appears to be a pulverulent highly-nitrogenous substance, which occurs along with the cardol and anacardic acid in the cellular spaces of the pericarp. It is partially dissolved by water to a mucilaginous liquid, and when heated with potash gives off a large amount of ammonia.

The medicinal effects of pure cardol far exceed those of the mixture extracted from the pericarp by æther. It is however not at all requisite that the cardol should be perfectly pure; the anacardium fruit merely requires, after being freed from the kernels and crushed, to be exhausted with alcohol and the extract digested with recently-

precipitated hydrated oxide of lead until no further action upon blue litmus-paper is perceptible. The greater portion of the alcohol is then distilled from the filtered liquid, and the residue mixed in a narrow cylinder with warm water, when the cardol separates as an oily stratum, which is easily removed into another vessel with a pipette. In this manner a valuable medicine is obtained, which with its moderate price is by no means inferior in its action to the expensive cantharidine, and moreover has the advantage of possessing a more permanent after-effect.—Liebig's *Annalen*, lxiii. p. 137.

Researches on Coffee Berries. By Dr. L. Rochleder.

The author had previously submitted the caffeo-tannic acid discovered by Pfaff along with caffeic acid in coffee berries to a more minute examination, and found that this acid in the presence of bases is modified by the oxygen of the atmosphere. Since caffeo-tannic acid is contained in the berries combined with bases, it must be supposed to experience in them a similar metamorphosis. Such changes must also occur on the germination of the berries. In the present treatise the author communicates the experiments he has made upon this subject.

The products of the metamorphosis of caffeo-tannic acid vary with the nature of the bases; those formed by ammonia differ from those produced by potash or soda; those which lime and baryta give rise to are at first identical with those produced by ammonia, but subsequently pass over into those generated by soda. The acid which originates from the caffeo-tannic acid in the presence of ammonia the author calls *viridic acid*. It is prepared in the following manner:—Pure caffeo-tannic acid is first obtained by exhausting dried pounded coffee-berries with boiling alcohol, mixing the decoction with water in order to separate the fat, and filtering, heating the filtered solution to boiling, and precipitating with solution of acetate of lead. The precipitate after washing is decomposed with sulphuretted hydrogen. If an excess of ammonia is added after driving off the sulphuretted hydrogen, dilute solutions become yellow, those that are more concentrated reddish-brown. On exposure to the air they absorb oxygen, become first greenish, and in the course of thirty-six hours bluish-green. After a long time this blue colour passes into a brown (even in sealed glass tubes in the course of a year and a half). If an excess of acetic acid be now added to the bluish-green liquid, when the colour changes to a chestnut-brown, and then alcohol, a substance separates resembling the metagallic acid of Pelouze or the japonic acid of Svanberg, but of which only a determination of the atomic weight could be made; it was found to be 2967. Separated from this black precipitate, the brown liquid now afforded with acetate of lead a greenish-blue precipitate of viridate of lead, whilst the yellow supernatant liquid still contained unaltered caffeo-tannic acid. The precipitate is suspended in hot water, and decomposed with sulphuretted hydrogen, when it affords an aqueous solution of viridic acid.

Viridate of Lead can also be obtained in the following manner:— The coffee-berries, which have been exhausted with alcohol, are extracted with water, and the extract precipitated with acetate of lead; the yellow precipitate is suspended in alcohol, and decomposed with sulphuretted hydrogen. Ammonia is added to the filtered liquid and exposed to the air for twenty-four hours, when it acquires a green colour; it is then mixed with twice its volume of alcohol of 0·951 spec. grav., and filtered from the greenish-blue precipitate which is formed. The precipitate is washed on the filter with alcohol, to which a minute trace of acetic acid has been added, then dissolved in acetic acid, and the organic substance again precipitated with acetate of lead in indigo-blue flakes. Dried at 212°, this lead salt afforded—

	I.			II.		
Carbon	31·77	14	= 32·61	31·37	14 = 1050·0	31·51
Hydrogen	2·33	6	2·33	2·81	7 87·5	2·63
Oxygen	21·15	7	21·75	23·95	8 800·0	24·01
Oxide of lead..	44·75	1	43·31	41·87	1 1394·5	41·85

I. is of the salt prepared according to the first plan, and II. of a salt obtained by the second method. According to the numbers, the salt I. was still mixed with a small quantity of a basic salt. If we subtract the amount of lead found from the weight of the substance analyzed, we must obtain the correct composition of viridic acid. The numbers deduced in this manner from analysis I. are—

Carbon.....	57·51	14	= 1050·0	57·54
Hydrogen	4·21	6	75·0	4·10
Oxygen	38·28	7	700·0	38·36

The solution of viridic acid obtained on decomposing the lead salt by sulphuretted hydrogen is of a brown colour. This solution leaves on evaporation an amorphous brown substance, which dissolves easily in water, and with a beautiful carmine-red colour in concentrated sulphuric acid, from which water again precipitates it in blue flakes. The aqueous solution of the acid affords with barytic water a bluish-green precipitate, which contained, when dried at 212°, 43·15 per cent. baryta; the formula $C^{14}H^{8}O^{9} + 2BaO$ requires 43·46 per cent. With soda and ammonia the aqueous solution of the acid immediately affords dark green liquids. Viridic acid communicates a greenish-blue colour to its salts. The green colour of the berries arises from viridate of lime. The mode of its formation may be represented by the following equation:—

$$\text{Caffeo-tannic acid } C^{16}H^{8}O^{7} - \text{viridic acid } C^{14}H^{6}O^{7} = (C^{2}H^{2} + xO).$$

In the production of viridic acid from caffeo-tannic acid no carbonic acid is evolved; the last member of the equation contains therefore those elements composing the above-mentioned black substance resembling metagallic acid. Viridic acid appears to be identical with Runge's green acid. Zwenger obtained in the dry distillation of pyrocatechine a substance which forms in the presence of

alkalies an acid becoming green by exposure to the air, and an oily body which is converted into resin in the air. The first substance agrees in its properties in a remarkable manner with caffeo-tannic and viridic acids. The composition of pyrocatechine is, according to Zwenger, $C^{18} H^9 O^6$; if we subtract from this the elements of caffeo-tannic acid, there remains, according to the author's statement, the carburetted hydrogen $C^2 H^2$, which is converted into resin in the air*.

Metamorphosis of the Viridates.—Viridate of ammonia turns brown by exposure to the air, but the acid does not appear to be altered, for the lead salt precipitated from this solution led to the formula $C^{28} H^{12} O^{14}$, PbO. Potash does not at first give a green solution with caffeo-tannic acid, but a brown one, from which alcohol separates the potash salt as a brown resinous mass. The salt dissolves with a brown colour in water, and furnishes with acetate of lead a brown precipitate. Acetic acid does not alter the solution. If the first solution of the caffeo-tannic acid with excess of potash has been slightly boiled, acetic acid throws down from the brown liquid a green precipitate. The aqueous yellow decoction of the berries of coffee changes into brown by exposure to the air, owing to the caffeo-tannate of potash dissolved in it.

Caffeic Acid.—It has been previously stated that this acid was discovered along with caffeo-tannic acid by Pfaff, whose mode of preparation the author followed, previously however treating the berries with hot spirit, that the water might more easily penetrate them. The aqueous decoction was then thrown down with acetate of lead, the precipitate washed and decomposed with sulphuretted hydrogen. If the solution separated from the sulphuret of lead is evaporated to a syrup, and poured in this state into alcohol, white flakes subside, which form on drying a white light powder. The aqueous solution becomes brown in the air, and yields with acetate of lead a white precipitate, which acquires, in drying at 212°, a greenish-gray colour. The author obtained 1½ grm. of this lead salt from a pound of coffee-berries. The pulverulent acid, as it is obtained after the addition of alcohol to its aqueous solution, diffuses on dry distillation the odour of roasted coffee more than any of the other ingredients of coffee. In a former paper the author stated that this acid afforded on analysis carbon and hydrogen in the same proportion as they are contained in caffeo-tannic acid, but that the oxygen could not be obtained constant. The following numbers contain the results of one out of several analyses; but it merely shows the relative value of the constituents:—

Carbon	12·32	16	12·40
Hydrogen	1·06	8	1·03
Oxygen	13·72	14	14·48
Oxide of lead	72·90	5	72·09

* It is however requisite to admit 1 equiv. water into the calculation, as the above formula for pyrocatechine, $C^{18} H^9 O^6$, only leaves $C^2 H^2$ after the addition of HO and subtraction of $C^{16} H^8 O^7$, although the expression $C^{18} H^9 O^6$ represents hydrated substance, as Zwenger's combination of oxide of lead with pyrocatechine = $C^6 H^2 O$ + PbO.—Ed. *Pharm. Centr. Blatt.*

Caffeine.—According to the results which the author has hitherto obtained, caffeine contains a portion of its carbon and nitrogen in the form of cyanogen. Heated with soda lime up to 356°, it parts with a sensible quantity of cyanogen to the bases, which morphine, quinine, cinchonine and piperine do not. The chloride of platinum and caffeine contains 24·6–24·5 per cent. platinum (these numbers agree perfectly with those obtained by Nicholson), showing that Payen's analysis cannot be correct. Boiled with nitric acid, a new double salt crystallizes from the hot solution on cooling in six-sided tablets. Dissolved in water and treated with nitrate of silver and evaporated, cyanate of silver is not formed, but a white crystalline compound of caffeine, oxide of silver and nitric acid, which detonates when heated with evolution of red vapours. On boiling with muriatic acid and chlorate of potash, and carefully evaporating, alloxane, or a body very similar to it, separates in crystals, the solution of which stains the skin red, and imparts to it a peculiar odour. Ammonia produces with it a solution of murexide, and protosalts of iron with an alkali produce an indigo-blue colour.—Liebig's *Annalen*, lxiii. p. 193.

On the Changes which Albuminous Substances undergo in the Stomach during Digestion. By Prof. MULDER.

I showed last year that the fibrine of the blood undergoes no change of composition by solution in muriatic acid and precipitation by carbonate of ammonia. The results of my analysis, employing in the present instance my last experiments on the amount of sulphur in these substances, were as follows:—

	Undissolved fibrine.	Fibrine dissolved and thrown down by carbonate of ammonia.
Carbon	52·7	52·7
Hydrogen	6·9	6·9
Nitrogen	15·4	15·8
Oxygen	23·5	23·5
Sulphur*	1·2	1·1
Phosphorus	0·3	

The phosphorus was not determined in the dissolved portion; but as vitelline loses phosphamide under the influence of acetic acid and ammonia, it is probable that fibrine will have been deprived of the phosphamide under the influence of the muriatic acid and carbonate of ammonia. The same experiments were made upon caseine and albumen, and the following results obtained:—

A small quantity of muriatic acid was added to milk; a precipitate fell, which was washed for a long time with water. At last the mass began to be gelatinous; in this state it was mixed with water, and set aside at a temperature of about 104° F. After some hours the whole was dissolved, and the butter rose to the top. The watery solution was decanted, thrown down by carbonate of ammonia, and the precipitate completely washed with water, alcohol and æther, and dried at 262° F. It yielded on analysis—

* The sulphur was determined by caustic soda and nitre.

	Undissolved caseine.	Dissolved and thrown down. I.	II.
Carbon	53·8	53·44	53·08
Hydrogen	7·1	7·01	6·93
Nitrogen	15·6	15·01	15·30
Oxygen	22·6	23·93	23·96
Sulphur	0·9	0·61	0·73

Caseine, as I have shown, as well as Schlossberger, is a complex body; it consists of different proteine compounds, of which the body that I have now studied constitutes the chief element; it is characterized by a somewhat smaller amount of sulphur, and is moreover distinguished from the mixture hitherto called caseine, by the circumstance that it contains more oxygen. It shows the reaction of sulphamide-proteine:—

		Without SNH^2.	
Carbon	53·5	53·4	54·1
Hydrogen	7·0	6·9	7·0
Nitrogen	15·0	14·5	14·7
Oxygen	23·9	23·9	24·2
Sulphur	0·6		
	100·0	98·7	100·0

Albumen of Eggs, coagulated by heat, was mixed with diluted muriatic acid, and after the addition of a small piece of rennet, set aside at a temperature of 104° F. After some days the albumen was completely dissolved. Carbonate of ammonia was added to the filtered liquid and the precipitate washed with water, alcohol and æther, and dried at 262° F.

	Undissolved albumen.	Dissolved and thrown down. I.	II.	Mean.
Carbon	53·5	52·74	53·11	53·0
Hydrogen	7·0	6·93	6·93	6·9
Nitrogen	15·5	15·97	15·60	15·8
Oxygen	22·0	22·53	22·63	22·5
Sulphur	1·6	1·83	1·73	1·8
Phosphorus	0·4			

The phosphorus, probably not contained in the precipitated albumen, was not determined. The quantity of sulphur exceeds that in albumen by 0·2 per cent.; however, I do not doubt that this increase must only be ascribed to an error of experiment. It showed, at any rate, the reaction of sulphamide:—

		Without SNH^2.	
Carbon	53·0	53·0	54·9
Hydrogen	6·9	6·8	7·0
Nitrogen	15·8	14·2	14·7
Oxygen	22·5	22·5	23·4
Sulphur	1·8		
	100·0	96·5	100·0

Thus albumen is not changed in composition as regards the carbon, hydrogen, nitrogen and oxygen and SNH^2; and it appears that no new combination of albumen is produced during the digestion in the stomach. Is this the case also with caseine? No other conclusion

can be drawn from the above analysis, than that either caseine contains already a substance richer in oxygen, or that the production of such a combination is caused during the solution in the stomach. Let us now compare the organic group which remains after deducting the elements of sulphamide from fibrine, hair, and this dissolved caseine:—

	Fibrine.	Hair.	Dissolved caseine.
Carbon	54·4	53·6	54·1
Hydrogen	7·0	7·1	7·0
Nitrogen	14·4	14·6	14·7
Oxygen	24·2	24·7	24·2

And let us place next to it the group occurring originally in caseine and albumen:—

	Caseine.	Albumen from eggs.	Albumen from blood.
Carbon	54·8	55·6	55·0
Hydrogen	7·1	7·1	7·2
Nitrogen	15·1	14·4	14·5
Oxygen	23·0	22·9	23·3

It will now easily be seen that there exists a considerable difference. In the three first groups is contained evidently less carbon and more oxygen. They are expressed by—

	Atoms.	Calculated.
Carbon	36	53·6
Hydrogen	54	6·7
Nitrogen	8	13·9
Oxygen	13	25·8

The first change of the albumen in the stomach is therefore only solution; that of the caseine may also be oxidation. I say *may be*, for it is possible that this group already pre-exists in caseine. This can only be determined with certainty when the other constituents of caseine shall have been further examined.

At all events, in caseine, after its solution in the stomach, the same organic group exists as in fibrine; and there is so far an intimate relation between fibrine and caseine. Caseine must easily produce fibrine, while albumen remains still albumen in the stomach, and probably undergoes no other change than in the proportion of sulphamide it contains.

The question now is, how far the use of milk will be advisable in inflammatory diseases? This question I address to medical experience, being far from establishing any opinion upon the numerical results of experiments.—*Edinb. Monthly Journ.*, Oct. 1847.

Contributions to the Chemistry of the Varieties of Catechu. *By* Prof. Delffs.

Along with the Bengal catechu, which forms dark reddish-brown cakes scattered over with the husks of rice, there now occurs pretty frequently in commerce, the so-called Bombay catechu, in large irregular pieces of a uniform blackish-brown colour and fatty lustre, and which contain leaves of a species of palm disseminated through their mass. As both kinds are derived from *Acacia Catechu*, the

difference between them must be owing to the mode of treating them on evaporation; perhaps the last kind has been somewhat burned. The catechu in square pieces has been rejected by the Prussian, and also by the Baden Pharmacopœia, as an artificial product, consisting of clay and some astringent extract, while it has been admitted by the Hamburg Pharmacopœia. The author has never been able to discover any considerable amount of alumina in it; moreover the same kind still occurs in commerce, only that the squares are caked together; but it agrees with the old article in its lower specific gravity, ready friability, and sparing solubility in water.

When Bengal catechu is treated in a displacement-apparatus with ordinary æther containing water, and the liquid which passes (which does not separate into two layers, as with galls) is evaporated under the air-pump, a thick yellow syrup is obtained, and subsequently a brittle, yellowish, shining, amorphous mass of catechu-tannic acid, which tenaciously retains a little of the æther. It readily absorbs so much moisture from the air as to deliquesce into a yellow syrup. Its aqueous solution yields with bichromate of potash a considerable brown precipitate, which does not dissolve in muriatic acid. The alkaline salts of the catechu-tannic acid exhibit the same high degree of variability as the corresponding compounds of querci-tannic acid. If an aqueous solution of catechu-tannic acid be exposed to the air in a shallow vessel, decomposition very soon ensues, with the separation of a voluminous fibro-crystalline silky mass, or small acicular needles, which may be obtained perfectly colourless by allowing the hot aqueous solution to cool under the air-pump and pressing the separated mass between filtering paper. The substance thus obtained is catechuic acid, and exhibits in its behaviour so great an analogy to gallic acid, that the name catechine may be dispensed with. The composition of the acid is still not accurately determined, as the analyses hitherto made differ considerably from one another. The substance employed by the author for analysis was dried *in vacuo* over sulphuric acid, and burnt with chromate of lead. It yielded—

Carbon	54·16	54·29	7 =	53·846
Hydrogen	5·29	5·57	4	5·128
Oxygen	40·55	40·14	4	41·026

As the salts of catechuic acid are very variable, the determination of the atomic weight does not lead to any certain result. Hagen obtained from the lead compound 62·19 per cent. oxide of lead, which corresponds tolerably well to the formula $C^7 H^3 O^3 + HO$. The formula $C^9 H^4 O^4$ may be deduced from Pelouze's analysis of catechu-tannic acid; we should have therefore

$$C^9 H^3 O^3 + 4O = C^7 H^3 O^3 + 2CO^2,$$

as in the formation of gallic acid from tannic acid.

The so-called Gambia extract yields when pounded but very little to cold water, and appears to be very poor in tannin. It dissolves for the greater part in hot water, and congeals on cooling to a dirty yellow pasty mass, which behaves exactly like catechuic acid. It is therefore very probable that both drugs are derived from the same plant.—*Journ. für Prakt. Pharm.*, xii. p. 162.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution of Taurine and a new Substance isomeric with it. *By* J. REDTENBACHER.

In a former paper* I announced the presence of sulphur in taurine. At the conclusion of that notice I observed, that when taurine is oxidized with caustic potash, and the residuary mass decomposed with dilute muriatic acid, sulphuretted hydrogen and sulphurous acid escape, while sulphur is deposited precisely as if pure sulphur had been treated with potash. It is this reaction which will enable us to obtain an insight into the constitution of taurine. When, for instance, taurine is dissolved in pure caustic potash, and the solution very cautiously and gradually evaporated to dryness, a moment occurs when pure ammoniacal gas is disengaged; the whole of the nitrogen of the taurine is given off at this period as ammonia. After some moments the disengagement of ammonia ceases; and if the reaction is now interrupted by allowing the mass to cool, the non-nitrogenous constituents of taurine are combined as acids with the potash. No blackening or any other alteration has occurred, from which any considerable destruction of the combination formed with the potash might be suspected. If the cold residuary potash-compound is decomposed with dilute sulphuric acid, pure sulphurous acid is disengaged without any elimination of sulphur or sulphuretted hydrogen; and if the liquid is distilled, the product contains, along with sulphurous, acetic acid, and the residue in the retort is pure sulphate of potash. I digested the distillate with peroxide of lead, distilled off the acetic acid, and prepared from it a silver salt, which agreed in all its properties with pure acetate of silver.

More than twenty years ago Gmelin detected acetate of ammonia in the products of the destructive distillation of taurine.

The sole products of this reaction are therefore acetic acid, ammonia and sulphurous acid; but if we consider them more accurately, they will be found to contain a complete explanation of the mode of arrangement of the elements of taurine. Heated cautiously with potash, the taurine parts with sulphur in the form of sulphurous acid; this proves that it is contained as sulphurous acid in taurine; for if it existed in the form of unoxidized sulphur or as hyposulphurous acid, sulphur would have been eliminated on decomposing the

* Chem. Gaz., vol. iv. p. 238.

potash compound; if it existed as sulphuric acid, no sulphurous acid ought to be disengaged; and the presence of hyposulphuric acid is excluded from the small number of atoms of oxygen, and by the considerations which follow.

Taurine contains therefore 2 atoms of sulphurous acid, and if we

deduct from taurine ..... $C^4\,NH^7\,O^6\,S^2$

2 atoms of sulphurous acid ..... $O^4\,S^2$

the elements of ..... $C^4\,NH^7\,O^2$ =

aldehyde-ammonia remain ..... $C^4\,H^3\,O + NH^3 + HO$.

In the reaction the ammonia escapes as gas, and the aldehyde is oxidized and combines with the potash as acetic acid. Taurine is consequently bisulphite of aldehyde-ammonia in about the same state of condensation as cyanate of ammonia in urea.

As no compound is known containing aldehyde-ammonia and sulphurous acid, the above view respecting the constitution of taurine might not appear probable to many readers; such a compound however really exists, but in a less condensed state than in taurine, and analogous to the cyanate of ammonia. When aldehyde-ammonia is dissolved in alcohol and sulphurous acid passed into it, the liquid becomes considerably heated, while the gas is absorbed in large quantity. On keeping the solution of aldehyde well cooled, as soon as the liquid begins to have an acid reaction, a white crystalline substance separates in large quantity. It may also be obtained by mixing the alcoholic solution of aldehyde-ammonia with alcohol saturated with sulphurous acid until the appearance of an acid reaction. It is collected on a filter, washed with strong alcohol, dried under the air-pump, and is now nearly pure if the aldehyde-ammonia was pure and contained no free ammonia. It forms white minute prismatic needles, which taste faintly but distinctly of sulphurous acid and aldehyde-ammonia, and has an acid reaction. It gradually alters in the dry state by exposure to the air, and at 212° and access of air it is decomposed, becoming yellow, then brownish, and losing considerably in weight, at the same time diffusing an odour of burnt taurine. On analysis the following results were obtained:—

			Calculated.			Taurine.
Carbon	19·08	19·41	4 = 300·0	19·2		19·28
Nitrogen	11·98	..	1	175·0	11·2	11·25
Hydrogen	5·66	5·97	7	87·5	5·6	5·73
Oxygen	..	..	6	600·0	38·4	38·04
Sulphur	25·79	25·30	2	400·0	25·6	25·70

This salt, with the formula $C^4\,NH^7\,O^6\,S^2$, is consequently isomeric with taurine, and its elements are arranged in it in the same manner, but in a looser state of combination; in fact, it is *bisulphite of aldehyde-ammonia*, as is proved by all its reactions. But the aldehyde exists in it in a condensed state, perhaps as elaldehyde or metaldehyde; for sulphurous acid, ammonia and aldehyde, as also aldehyde-ammonia, are all volatile bodies, while their combination is no longer volatile. When heated upon platinum foil, it turns

brown, then black, puffs up, disengages an odour similar to burnt taurine, and leaves a porous cinder. When heated in a sealed tube to 212°, it appears to experience little alteration; at 242°–284° it becomes yellowish, and on breaking the tube the odour of sulphurous acid is very distinct. This salt dissolves readily in water, but it is not easy to crystallize it from it, for on evaporating the solution *in vacuo* but few crystals are formed, the greater portion remaining as a tenacious gummy mass. It likewise dissolves in spirit, but with difficulty in absolute alcohol; the spirituous solution behaves like the aqueous solution on evaporation *in vacuo*. If the spirit is partially distilled from an alcoholic solution, it contains sulphurous acid. On mixing a very saturated solution of this salt with an excess of very strong alcohol, a thick syrupy substance separated at the bottom without the production of crystals, a few of which were formed only after a very long interval. I found it impossible therefore to recrystallize it.

When the salt is mixed with a very strong acid, it disengages sulphurous acid, and the odour of aldehyde is perceptible; the residue is an ammonia salt of the acid. Heated with potash, it behaves like aldehyde towards potash. Salts of baryta, lead and silver yield with a solution of the salt precipitates, which dissolve partially or entirely in acids. The precipitate with nitrate of silver, which did not blacken, contained a mere trace of an organic body, and left on ignition more silver than neutral sulphite of silver would have done. All attempts to condense this bisulphite of aldehyde-ammonia into taurine were unsuccessful; perhaps some one else may prove more fortunate. Our knowledge of the latter substance is, at all events, advanced a step further, and we are enabled to form a correct idea of its constitution.—Liebig's *Annalen*, Jan. 1, 1848.

On Boheic Acid and its Salts, and on the Tannic Acid of the Leaves of Thea Bohea. *By* Dr. Rochleder.

In continuing his examination of the substances containing caffeine, Dr. Rochleder has likewise examined tea as to its constituents, in order to ascertain the relations which exist between the caffeine and the substances accompanying it. The leaves were exhausted with boiling water, and the boiling hot neutral brown extract precipitated with acetate of lead. The dark grayish-brown precipitate contained tannate of lead and a little boheate of lead, besides the lead compounds of such substances which have originated from the decomposition of the two preceding acids, and which are probably entirely absent in the fresh leaves. The yellow liquid filtered from the lead precipitate deposits in the course of twenty-four hours some crystals of a lead salt, which appear under the microscope to be four-sided prisms, and after ignition leave a residue of lead of the same form. The liquid decanted from this sediment yields, on the addition of a few drops of ammonia or of tribasic acetate of lead, a yellow flocculent precipitate, upon the subsidence of which the liquid appears colourless, and contains mere traces of other substances.

Tannic Acid.—It is stated by Mulder that the tannic acid of tea differs in none of its properties from quercitannic acid. This statement is confirmed by the author. It is obtained from the previously-mentioned grayish-brown precipitate by suspending it in water and decomposing it with sulphuretted hydrogen. The liquid filtered from the sulphuret of lead contains, besides the tannic acid, some boheic acid, and a very small quantity of another acid, while the brown products of decomposition are held back by the sulphuret of lead. The liquid is concentrated over sulphuric acid *in vacuo*, and absolute alcohol added to it, which precipitates a small portion of a mucilaginous substance. The alcohol is then again evaporated over sulphuric acid, the residue dissolved in a little water, and the solution agitated with æther, which dissolves the crystalline acid and some tannic acid. The aqueous solution of tannic acid then dries *in vacuo* over sulphuric acid to a faintly yellow mass, which cannot be distinguished in its properties from quercitannic acid. The aqueous solution was precipitated with a solution of acetate of lead, and the lead precipitate analysed. The analysis of substance dried over sulphuric acid *in vacuo* gave—

Carbon	50·40	18	50·94
Hydrogen	4·20	8	3·78
Oxygen	45·40	12	45·28

In a second preparation, a boiling solution of tannic acid was mixed with a boiling solution of acetate of lead, and kept in ebullition for a quarter of an hour, upon which the precipitate was collected on a filter, washed and dried. In this state it contained 64·49 per cent. oxide of lead, while the precipitate which is obtained under the same conditions with tannic acid from galls contains 64·00 per cent.; there is no doubt therefore that the tannic acid of the tea is identical with quercitannic acid.

Boheic Acid.—The previously-mentioned yellow precipitate contains boheate of lead. In preparing the acid for analysis, the decoction of the leaves was precipitated with acetate of lead, filtered from the grayish-brown precipitate, and the liquid set aside for twenty-four hours. The liquid, after being separated from the additional slight precipitate, afforded with ammonia a yellow precipitate; this was mixed with absolute alcohol, decomposed with sulphuretted hydrogen, freed from sulphuretted hydrogen *in vacuo* over a concentrated solution of potash, and then precipitated with an alcoholic solution of acetate of lead. Dried at 212° it has a somewhat grayish colour. On analysis it afforded—

Carbon.....	21·33	7 =	525·0	20·33
Hydrogen	2·68	5	62·5	2·42
Oxygen	23·99	6	600·0	23·24
Oxide of lead	52·00	1	1394·5	54·01

If we deduct from these results 52 per cent. oxide of lead, and calculate the composition of the organic substance combined with the lead, we obtain—

Carbon.....	44·45	7 =	525·0	44·21
Hydrogen	5·59	5	62·5	5·26
Oxygen	49·96	6	600·0	50·53

Another lead salt of boheic acid was prepared as above, but then formed into a paste with absolute alcohol, and decomposed with sulphuretted hydrogen. The liquid filtered from the sulphuret of lead was dissolved in water, and precipitated with an ammoniacal solution of acetate of lead. The yellow precipitate thus obtained possessed, when dried at 212°, the following composition:—

Carbon.....	14·01	7 =	525·0	13·58
Hydrogen	1·39	4	50·0	1·29
Oxygen	..	5	500·0	12·95
Oxide of lead	71·43	2	2789·0	72·18

If we deduct from the results of this analysis the amount of lead in the salt, we obtain as the composition of the organic substance—

Carbon.....	49·02	7 =	520·0	48·84
Hydrogen	4·85	4	50·0	4·65
Oxygen	46·13	5	500·0	46·51

In preparing the baryta salt of boheic acid, the aqueous acid separated from the lead precipitate was mixed with alcohol, and then with so much barytic water until a faint alkaline reaction was perceptible. The precipitate was collected on a filter, access of air prevented, and washed with water containing spirit. On analysis the author found—

Carbon.....	24·32	7 =	525·0	24·48
Hydrogen	3·08	5	62·5	2·91
Oxygen	28·30	6	600·0	27·99
Baryta.....	44·30	1	957·0	44.62

The hydrate of boheic acid was obtained by decomposing boheate of lead mixed with absolute alcohol with sulphuretted hydrogen, evaporating the liquid filtered from the sulphuret of lead *in vacuo*, dissolving the residue in water, and again evaporating *in vacuo*; the residue was then dried at 212°. This process was repeated three times; the substance was then left for three weeks *in vacuo*. In this state boheic acid forms a pale yellow mass resembling tannic acid; it melts at 212° to a red substance, which may be drawn out into threads, and quickly absorbs water, so that it becomes adhesive after a few minutes' exposure to the air. This is the reason of the hydrogen being rather too high, as the substance cannot be mixed hot with oxide of copper. The analyses made with this substance gave—

Carbon.....	44·2	7 =	525·0	44·2
Hydrogen	5·8	5	62·5	5·3
Oxygen	50·0	6	600·0	50·5

Besides the compounds here described, the author obtained a lead salt, the analysis of which led to the formula $C^7 H^3 O^4, PbO$, but which could not be again obtained. The formulæ for the boheates are as follows:—

$$PbO, C^7 H^5 O^6 = PbO, C^7 H^3 O^4 + 2HO$$
$$2PbO, C^7 H^4 O^5 = 2PbO, C^7 H^3 O^4 + HO$$
$$PbO, C^7 H^3 O^4 = PbO, C^7 H^3 O^4$$
$$BaO, C^7 H^5 O^6 = BaO, C^7 H^3 O^4 + 2HO$$
$$C^7 H^5 O^6 = C^7 H^3 O^4 + 2HO$$

Boheic acid possesses, like all the acids of the formula $C^{2m} H^{m-1} O^n$, the property of colouring persalts of iron dark; however, it produces no precipitate in a solution of the perchloride of iron. It is soon altered by exposure to the air. On dry distillation it yields a liquid which smells of acetic acid and produces a black colouring with persalts of iron. The quantity of this acid in tea is very small; 1 lb. afforded only 1·5 grm. of lead salt. From the above composition it is seen how closely related it is to gallic acid and kinic acid; boheic acid = $C^7 H^3 O^3$, kinic acid = $C^7 H^4 O^4$, gallic acid = $C^7 H^2 O^3$. Since tea contains tannic acid, it is not at all improbable that, by its transition into gallic acid, and subsequent assimilation of 1 equiv. water and elimination of 1 equiv. oxygen, boheic acid is formed from the tannic acid in the tea plant, $C^7 H^2 O^4 + HO - O = C^7 H^3 O^4$. The viridic acid, discovered by the author, and which he found to be a product of oxidation of caffeo-tannic acid, is represented by the formula $C^{14} H^6 O^7$; the doubled formula of boheic acid = $C^{14} H^6 O^8$ differs from viridic acid only by 1 equiv. more oxygen.—Liebig's *Annalen*, lxiii. p. 202.

On the Fatty Acids of Castor Oil. By M. Saalmuller.

The author has submitted the fatty acids which are formed on the saponification of castor oil to a more accurate examination. The latest researches upon this subject were made by Bussy and Lecanu, who admit as the products of saponification, glycerine and three acids, margaritic, elaiodic and ricinic acids, the first of which is solid, while the two latter are liquid. The author obtained a solid substance, agreeing in its properties with margaritic acid, but differing by a larger amount of carbon; and he points out with great probability the reason of the carbon having fallen out too low in the analyses of Bussy and Lecanu. Instead of two fluid acids, he obtained only one, ricinoleic acid, which constitutes by far the greater portion of the saponified oil.

Bussy and Lecanu decomposed castor oil by saponification with alkalies into the above-mentioned fatty acids. From the solution of these acids in alcohol the solid acid to which they applied the name of margaritic separates in small quantity. What remains in the solution is considered by them to be identical with the acid product which is obtained in the destructive distillation of castor oil, on which account they assume the two peculiar acids, ricinic and elaiodic acids, found in the distillate, to be likewise present in the liquid product of the saponification, as both substances solidified at 21° F. dissolved in solution of potash, reddened blue litmus, and formed with magnesia, oxide of lead, and other metallic oxides, salts soluble in alcohol.

On decomposing the soap, produced by treating castor oil with potash or soda, with muriatic acid or tartaric acid, the author obtained glycerine and a mixture of fatty acids liquid at the ordinary temperature, and from which a small quantity of solid margaritic acid separated, but which was obtained in far greater abundance by dissolving the eliminated fatty acids in alcohol, and exposing this solution for some length of time to a temperature of 14° −10° F. After repeated recrystallization from alcohol, this substance possessed a remarkably high melting-point; Bussy and Lecanu state it to be 266°. The author found it at first still higher, but he observed that it sunk with each fresh recrystallization until it remained constant at 165°. Only after the acid had acquired this melting-point did it burn without any residue. It is therefore probable that the high melting-point of the product obtained by Bussy and Lecanu was owing to some alkali tenaciously adhering to it. The author obtained but minute quantities of this acid, so that it was impossible to prepare its salts and determine its composition more accurately. From the properties just mentioned of a substance containing alkali, and the high melting-point stated by the French chemists, the author concludes that the acid analysed by them likewise contained alkali, which accounts for too little carbon being obtained. The acid, which the author purified perfectly from alkali, melted at 165°; but this, after it had been melted several times, sunk to 158°, and the point of solidification likewise fluctuated between 155° and 158°. In this respect, and in its composition, it exhibits a great resemblance to stearic acid, as will be seen from the following analysis, compared with the composition of stearic acid, $C^{68}H^{68}O^{7}$, I. being the results obtained by the author, II. those obtained by Bussy and Lecanu:—

	I.	II.	Stearic acid.
Carbon	76·85	70·50	76·69
Hydrogen	12·74	10·81	12·76
Oxygen	10·41	18·69	10·55

The author obtained less carbon with a margaritic acid which had been prepared from a different sample of castor oil, its composition approaching more to that of palmitic acid, $C^{32}H^{32}O^{4}$. The melting-point however remained constant, and differed therefore from the latter acid (140°–144°). The acid is volatilized when heated upon platinum-foil, and afforded on analysis the following numbers:—

				Palmitic acid.
Carbon	74·74	74·64	74·61	75·00
Hydrogen	12·88	12·62	12·46	12·50
Oxygen	12·38	12·74	12·93	12·50

Ricinoleic Acid.—The solution of the other fatty substance, which had been separated by pressure from the margaritic acid, became entirely solid at a low temperature when the alcohol had evaporated. This body could not be separated by any means into two or more different acids. When warmed with an excess of oxide of lead, it forms a white plaster, which is almost wholly soluble in

æther. When this ætherial solution is decomposed with muriatic acid, and water then added to separate the fatty acids, there remains, when the water has evaporated, a brownish-yellow liquid fatty acid, which is obtained pure in the most simple manner by the process proposed by Gottlieb for purifying oleic acid. The substance is saponified with an excess of ammonia, then precipitated with chloride of barium, and the dazzling white baryta salt dried upon a plate of plaster of Paris. The dried baryta salt is now dissolved at a gentle heat in strong alcohol, taking care that it does not melt to a tenacious brown mass. From this solution it soon separates on cooling in minute granular crystals, which are several times recrystallized from alcohol. In this manner a baryta compound is obtained of constant composition, and the fatty acid separated from it always possessed the same properties; for which reason the author does not regard this acid, with Bussy and Lecanu, as a mixture of ricinic and elaiodic acids, but as a single acid, for which he retains the name of ricinoleic acid.

Preparation and Properties of the pure Acid.—The baryta compound, prepared as above described, is decomposed with muriatic acid, and the eliminated mass washed with water containing muriatic acid as long as any baryta is removed, as the last portions of baryta are held back with considerable tenacity by the ricinoleic acid. In this decomposition of the salt the use of alcohol must be avoided; otherwise the acid can scarcely be obtained free from spirit, even when warmed for several days in the water-bath and a current of dry carbonic acid gas passed through it.

Pure ricinoleic acid forms at the ordinary temperature a syrupy pale yellow liquid, which is colourless in thin layers, has a very strong and most disagreeable acrid taste, but is perfectly void of smell. Its specific gravity is 0·940 at 59°; between 21° and 14° it solidifies to one mass of spherical aggregations; it may be mixed in every proportion with alcohol and æther; the alcoholic solution has a decidedly acid reaction, and decomposes the carbonated alkalies with effervescence. It does not absorb oxygen from the atmosphere at the ordinary temperature. Ricinoleic acid cannot be distilled without decomposition; the first products are very liquid; those which follow are quite thick and of a disagreeable odour; sebacic acid could not be detected in it, any more than in the products of the dry distillation of the oil itself, a fact which had been already observed by Bussy and Lecanu. The salts of ricinoleic acid are, with the exception of those with the alkalies, for the greater part crystalline, and, like the acid itself, not altered by exposure to the air.

The acid employed in the following analyses was dried for a considerable time over sulphuric acid. A sample, heated moderately in a glass tube, no longer gave any deposit of moisture. It was requisite to employ oxygen in the combustion. The hydrate water of the acid is expelled on its combination with oxide of lead. It lost, when heated with oxide of lead, 3·6 and 2·9, or on the average 3·25 per cent. of water. The hydrated acid was burnt, and the results are

given under I. and II. Annexed is the calculated composition of the anhydrous acid; whence it will be seen, on comparing the amount of hydrogen and oxygen, that the hydrated acid must, on losing its hydrate water, decrease 2·90 per cent., which closely agrees with the results above mentioned:—

	I.	II.	(H=1)			Anhydrous acid.		
Carbon	73·06	73·16	38	=228	73·08	38	=228	75·25
Hydrogen....	11·68	11·59	36	36	11·54	35	35	11·55
Oxygen.....	15·26	15·25	6	48	15·38	5	40	13·20

Ricinoleate of Baryta, BaO, $C^{38} H^{35} O^5$, is procured, as stated in the preparation of the acid, by supersaturating the acid, as it is obtained on decomposing the ricinoleate of lead dissolved in water, with ammonia, diluting the liquid with a large quantity of water, and precipitating with chloride of barium. The salt falls in caseous flakes, which are washed with water, and after being gently dried, dissolved in alcohol. From this solution it crystallizes in delicate plates, which are dried *in vacuo* over sulphuric acid. In this, as in most of the following salts, a portion of the salt remains behind in the form of a tenacious yellow mass. The analysis was made with the addition of phosphate of copper, and afforded—

Carbon.....	59·93	59·60	60·03	38	=228·0	60·06
Hydrogen	9·32	9·60	9·26	35	35·0	9·24
Oxygen	10·52	10·55	10·60	5	40·0	10·47
Baryta.....	20·23	20·25	..	1	76·6	20·23

Ricinoleate of Strontia, SrO, $C^{38} H^{35} O^5$, is obtained by precipitating dilute ricinoleic acid, to which excess of ammonia has been added, with chloride of strontium. It crystallizes from alcohol in small white granules. On ignition with sulphuric acid, it left 25·9 per cent. sulphate of strontia = 14·61 strontia; consequently the salt consists of—

$C^{38} H^{35} O^5$	85·39	1	= 303	85·36
Strontia	14·61	1	52	14·64

Ricinoleate of Lime, CaO, $C^{38} H^{35} O^5$ + HO (at 212°), is obtained by precipitating ricinoleate of ammonia with chloride of calcium, and recrystallizing from alcohol in minute, scaly, dazzling white crystals, which part with water on fusion even after they have been dried for a very long time *in vacuo* over sulphuric acid. These crystals melt at 176° to a transparent pale yellow mass, which after cooling is brittle and readily reduced to powder. The analyses afforded—

Carbon.....	66·33	66·42	38	= 228	67·06
Hydrogen	10·53	10·66	36	36	10·59
Oxygen	14·67	14·48	6	48	14·11
Lime	8·47	8·44	1	28	8·24

Ricinoleate of Magnesia, MgO, $C^{38} H^{35} O^5$, crystallizes from alcohol in fine needles. It dissolves very readily in this liquid, and is

rendered anhydrous by drying over sulphuric acid. The salt left on ignition 5·69 per cent. magnesia. The above formula requires 6·19.

Ricinoleate of Zinc, ZnO, $C^{38}H^{35}O^5$, crystallizes from a solution in alcohol in white granules. It left on ignition 11·85 per cent. oxide of zinc. The above formula requires 11·69.

Ricinoleate of Lead, PbO, $C^{38}H^{35}O^5$.—On digesting pure ricinoleic acid with finely powdered oxide of lead, a solid mass is soon formed, which dissolves readily in æther. The solution leaves, on evaporation over sulphuric acid, a crystalline transparent residue, which melts at 212° to a light brownish tenacious liquid, and is easily reduced to powder on cooling. In this manner the acid obtained in different preparations is constant, which is not the case when prepared by precipitating the basic ammoniacal salt with acetate of lead. The following analyses were made with a substance which had been crystallized from æther and dried over sulphuric acid, or melted at 212°:—

Carbon	54·45	54·75	54·35	38	= 228	54·94
Hydrogen	8·65	8·73	8·45	35	35	8·43
Oxygen	9·82	9·89	9·76	5	40	9·55
Oxide of lead	27·08	26·83	27·44	1	112	27·08

Ricinoleate of Silver, AgO, $C^{38}H^{35}O^5$, is not easily obtained of constant composition. A salt, which had been prepared from ricinoleate of ammonia, with a great excess of base, by the addition of dilute nitrate of silver, afforded on analysis, after desiccation over sulphuric acid—

Carbon.....	54·01	53·76	38	= 228	54·41
Hydrogen	8·42	8·32	35	35	8·37
Oxygen	10·08	10·43	5	40	9·54
Oxide of silver ..	27·49	27·49	1	116	27·68

Ricinoleate of the Oxide of Ethyle, C^4H^5O, $C^{38}H^{35}O^5$, is formed, under the influence of muriatic gas, from the solution of ricinoleic acid in absolute alcohol. The crude product is first washed with water containing a little carbonate of soda, and then with distilled water. It forms after this treatment a pale yellow oily liquid, which can be distilled without decomposition. The analysis gave—

Carbon.....	73·87	42	= 252	74·12
Hydrogen.....	11·76	40	40	11·76
Oxygen.....	14·37	6	48	14·12

The fatty acid liquid at the ordinary temperature, and which forms the principal constituent of castor oil, differs, according to this investigation, from oleic acid; it contains 1 atom more of each of the three elements than oleic acid, according to Gottlieb, which is $C^{37}H^{33}O^3 + HO$, while ricinoleic acid is $C^{38}H^{35}O^5 + HO$.

Among the products of distillation of ricinoleic acid, the author could not detect sebacic acid any more than Bussy and Lecanu (in the supposed mixture of ricinic and elaiodic acid). This appears to be in some way related to the property which ricinoleic acid possesses of absorbing no more oxygen by exposure to the atmosphere, and it must consequently be saturated with it. Boudet has asserted,

as a general property of the fatty oils, that they are rendered solid by sulphurous acid in the same manner as by nitrous acid. Sulphurous acid has no action upon castor oil nor upon the purified acid.—Liebig's *Annalen*, lxiv. p. 108.

On Carbothialdine, a new Base containing Sulphur. *By* Prof. J. Redtenbacher *and* Prof. J. Liebig.

When pure aldehyde-ammonia is dissolved in alcohol, and sulphuret of carbon added to the mixture, it immediately loses its alkaline reaction, becomes slightly warm, and in a few minutes deposits shining white crystals, which washed with a little alcohol constitute pure carbothialdine. This body is nearly insoluble in water and in cold æther, difficultly soluble in cold, but readily in boiling alcohol, from which it crystallizes without change; it forms a very weak organic base, containing sulphur, but no oxygen.

When crystallized carbothialdine is treated with dilute muriatic acid, it instantly disappears; a colourless solution is obtained, in which ammonia and alkalies instantly produce a crystalline precipitate, which is unaltered carbothialdine; but if set aside for a time at the ordinary temperature, it gelatinizes to a yellowish-white paste, insoluble in water; boiled with an excess of muriatic acid, it is decomposed into chloride of ammonium, sulphuret of carbon and aldehyde. When to a hot solution of carbothialdine in alcohol oxalic acid and æther are added, very slender white crystals of oxalate of ammonia separate immediately. An alcoholic solution of carbothialdine produces a greenish-black precipitate in a solution of silver, which very soon becomes black, and is converted into sulphuret of silver. Corrosive sublimate is precipitated in dense yellowish-white caseous flakes; copper salts form a thick green precipitate. The analysis of this substance led to the following results:—

Carbon	36·87	5 =	30	37·04
Nitrogen	17·16	1	14	17·28
Hydrogen	6·39	5	5	6·17
Sulphur	39·64	2	32	39·51

The formation of carbothialdine is readily explained. When 1 equiv. sulphuret of carbon is added to the elements of aldehyde-ammonia, and 2 equivs. water removed, we obtain precisely the composition of this organic base.—Liebig's *Annalen*, Jan. 1848.

On the Products resulting from the Putrefaction of Animal Caseine. *By* P. Iljenko.

This paper forms a continuation of one published some time ago by the author in conjunction with M. Laskowski on this subject. In their former investigation they found valerianic acid to be one of the products. Subsequently Liebig showed that valerianic acid and leucine were obtained on fusing caseine with hydrate of potash. In the present notice the author shows that, on the putrefaction of caseine in water, butyric and valerianic acids are formed, that a por-

tion of the caseine is dissolved in the liquid by the ammonia which is produced, and moreover that leucine is probably contained in the solution.

In preparing the caseine for the following experiments, the author first employed the method proposed by Figuier for the analysis of the blood. Fresh skimmed milk was saturated with common salt, and after standing for some hours, filtered through linen and paper. The whole of the fat is left on the filter, while the other constituents of the milk are contained in the clear yellowish solution. On boiling this, the caseine separates in white flakes, which are easily freed by washing with hot water from adherent chloride of sodium and milk-sugar. The caseine thus prepared was always perfectly free from fat, but contained a large quantity (about 11·8 per cent.) of inorganic constituents. This method proved very satisfactory when the quantities operated upon were not large, as in the following investigation, in which 100 lbs. were experimented on.

In preparing so large a quantity, Rochleder's method is preferable. Fresh cheese, prepared by the spontaneous curdling of the milk, was washed with water, then dissolved without heat in carbonate of soda, and set aside for twenty-four hours. The fat which had collected on the surface was removed, upon which the caseine was precipitated with sulphuric acid from the clear solution, and deprived of the last traces of fat by treatment with alcohol and æther. 8 lbs. of pure caseine, prepared in this manner, were mixed with distilled water, and exposed to the action of the air at a summer temperature.

There was no evolution of gas after the lapse of a week, but the mass began to smell, and the liquid had a faint alkaline reaction. Soon after, gas began to be disengaged, and the smell became very strong and disagreeable; at the same time a gas was given off, consisting of carbonate of ammonia and sulphuret of ammonium. For three weeks, during which time the liquid was decanted every three or four days and replaced by fresh water, the evolution of these gases continued, and the liquids remained alkaline. After two months and a half the mass of caseine had diminished considerably. All the liquids were united, as the several portions behaved similarly towards reagents. After filtration they were transparent, of a yellowish colour, and afforded with acetic acid a flocculent white precipitate. When boiled with alcohol and sulphuric acid, the odour of the æther of the volatile fats was immediately perceptible.

Volatile Products.—I. *Volatile Oil.*—On supersaturating the above liquid with sulphuric acid, filtering from the precipitate thus produced, and distilling, a product passed over, in which butyric and valerianic acids were immediately detected by their odour. It contained moreover a volatile oil of a peculiar odour, which was separated in the following manner from the volatile acids. The acid distillate was saturated with bicarbonate of soda, and evaporated in a retort. The acids combined with soda constituted the residue in the retort, while the oil passed over with the water, in which it remained dissolved. When this water was boiled with some sulphuric or nitric acid, it turned brownish-yellow, and on boiling with

muriatic acid it acquired a rosy tint. On agitation with a large quantity of æther, the oil is removed; the ætherial solution is perfectly colourless. Removed from the aqueous liquid, and the æther evaporated spontaneously, the residue was a brown-coloured oil of a very disagreeable odour. When redissolved in æther, the solution was no longer colourless, but yellowish-brown, a change which the oil can only have experienced by contact with the air. In this modified state it has retained its volatility, is insoluble in water, and soluble in æther and in alcohol. On adding water to the alcoholic solution, it is rendered turbid by the separating oil. It appears in this state to possess acid properties, for it dissolves in potash to a yellowish liquid. It was impossible to examine this oil more minutely.

2. *Butyric Acid.*—The residue in the retort, consisting of the soda salts of the volatile acids, was now decomposed with sulphuric acid and distilled. The product was saturated with carbonate of baryta, evaporated to dryness, and treated with a very little hot water, in order to separate the more readily soluble butyrate from the valerianate of baryta. This solution subsequently deposited small granular crystals, which were dried at 212° and burnt; the following are the results:—

Carbon.....	31·11	30·98	8 =	600·00	30·89
Hydrogen.....	4·59	4·30	7	87·50	4·50
Oxygen.....	15·47	15·65	3	300·00	15·45
Baryta	48·83	49·07	1	954·85	49·16

3. *Valerianic Acid.*—After removing the butyrate of baryta in the manner above described, the residue was dissolved in hot water; but as no crystals could be obtained from the concentrated ley, it was again evaporated to dryness, the dry residue treated with a quantity of water not sufficient to dissolve it, and the insoluble residue separated from the liquid. On analysing this substance, the composition of the valerianate of baryta was found, viz.—

Carbon.....	35·12	10 =	750·00	35·42
Hydrogen	5·42	9	112·50	5·31
Oxygen	13·82	3	300·00	14·18
Baryta.....	45·64	1	954·85	45·09

On one occasion the author obtained only butyric acid among the products of putrefaction of caseine, although under perfectly identical circumstances.

Non-Volatile Products.—1. *Caseine.*—It has already been stated that acids precipitate a body in white flakes from the liquid decanted from the putrefying caseine. The properties of this substance agree perfectly with those of caseine. Absolute alcohol also produces a precipitate of caseine. The caseine is held in solution in the liquid by the ammonia which is formed during the putrefaction. The precipitate thrown down by acetic acid, dried at 242°, left on incineration 4·3 per cent. ash, and yielded on analysis the numbers under No. I., which are compared with Mulder's analysis of caseine:—

	I.	According to Mulder.
Carbon	53·69	54·207
Hydrogen	7·02	7·160
Nitrogen	15·03 and 15·65	15·618
Oxygen Sulphur	"	

2. *Leucine.*—According to Proust and Braconnot, the fixed substance which is formed in the putrefaction of caseine, is principally oxide of caseum or aposepedine. To obtain this from the above liquid, the latter was evaporated in a retort according to Braconnot's directions, separated from eliminated caseine, and concentrated to a syrupy consistence. In this state the residue formed a brown extract, which did not solidify as asserted by Braconnot. On adding alcohol to it, a white pulverulent residue remained, and the alcohol assumed a yellow colour. The residue, after further washing with alcohol, was obtained tolerably white; it dissolved in water, but did not agree in its properties with the aposepedine described by Braconnot. Tincture of galls precipitated the substance from the aqueous solution, and when in excess redissolved the precipitate; but sulphate of iron, chloride of calcium, chloride of barium and chloride of platinum afforded precipitates, which they are said not to do with aposepedine. From the first portions of alcohol with which the syrupy solution had been treated, a small quantity of laminar crystals separated, which were very readily soluble in water. They contained 10·42 per cent. nitrogen, which nearly agrees with the amount of nitrogen in leucine. The author is therefore of the same opinion as Mulder, and considers aposepedine to be nothing more than impure leucine. In the present instance it certainly contained caseine mixed with it. It must also be remembered that Liebig obtained leucine and valerianic acid on fusing caseine with potash.—Liebig's *Annalen*, lxiii. p. 264.

On the Action of Nitric Acid upon Brucine.
By S. G. Rosengarten.

Gerhardt asserts that nitrous æther is obtained on treating brucine with nitric acid, while Liebig, on repeating the experiment, obtained a liquid with properties different from those of nitrous æther. Recently Laurent has examined the subject; he operated upon 15 grms. of brucine, and let the gas which was evolved pass over lime, upon which he condensed it by means of a frigorific mixture. In this manner he obtained 1 grm. of a very mobile liquid, lighter than water, and which possessed the odour of nitrous æther. The liquid was rectified at a temperature which did not exceed 50°, upon which it was submitted to analysis. The analysis afforded 29 per cent. carbon and 6 per cent. hydrogen; nitrous æther contains 32 per cent. C and 6·6 H. Notwithstanding the great difference of 3 per cent. in the amount of carbon, these results nevertheless, in Laurent's opinion, justify the conclusion that the gas evolved in the action of

nitric acid upon brucine, at the ordinary temperature, is nitrous æther.

When the action of the nitric acid at the ordinary temperature is terminated, the residue is an orange mass; and Laurent states that he succeeded in crystallizing it. This substance, which Laurent calls *cacotheline*, gave on analysis (the results are not enumerated) numbers which led to the formula $C^{42} H^{22} N^4 O^{20}$. When 3 equivs. nitric acid are added to 1 equiv. brucine, and we subtract 1 equiv. nitrous æther and 2 equivs. water, the formula of cacotheline remains.

The great difference in the composition of the volatile product from that of nitrous æther rendered a further examination desirable. To obtain the liberated gas, fused brucine was mixed in a small retort with nitric acid of 1·4 spec. grav. in the cold; a violent disengagement of gas resulted, with evolution of heat; red vapours appeared, but in very minute quantity. The gas was first passed through a tube two feet long, filled with hydrate of lime, and then through one of the same length containing chloride of calcium. The gas burnt with a green flame, coloured a solution of iron immediately black, and was absorbed with remarkable ease by concentrated sulphuric acid; the sulphuric acid gradually assumes a beautiful blue colour, which after a time passes into a reddish one.

When a few drops of water were added to the acid, a violent evolution of gas immediately resulted, and red vapours made their appearance, accompanied by the odour of nitrous acid. From want of ice and the high temperature during the last summer, all attempts to condense the gas were in vain; it was therefore analysed by connecting a long combustion-tube with the preceding apparatus. The tube was provided, as usual, with the chloride of calcium and potash apparatus, and filled partly with recently-ignited copper turnings, and partly with oxide of copper. Every caution was employed to get rid of hygroscopic moisture. In one experiment, with 10 grms. brucine, the author obtained 0·3167 carbon and 0·0799 hydrogen, which in equivalents is in the relation of 4 : 6·05. In a second experiment with 6 grms. brucine, the relation was found to be as 4 : 6·38. This is far removed from the relative quantity of carbon and hydrogen in the æthers, and it is quite certain that the reaction is not so simple as stated by Laurent and Gerhardt.

A portion of the residue was treated with alcohol; the colour on drying was reddish-yellow, and not at all beautiful. On analysis it afforded—

Carbon	51·68	51·86
Hydrogen	5·44	5·51
Nitrogen.....	13·58	
Oxygen	29·30	

Laurent observes that he succeeded in crystallizing this body; but he does not describe by what method. The only method by which I could obtain any considerable quantity in crystals was by dissolving it in water strongly acidified with nitric acid. The cacotheline then crystallized in beautiful yellow laminæ, and on analysis afforded—

			$C^{42}H^{22}N^4O^{20}$
Carbon	51·57	51·50	51·43
Hydrogen	4·75	4·80	4·48
Nitrogen.....	12·69	..	11·43
Oxygen	30·99	..	32·66

A solution of this substance, mixed with nitrate of ammonia and silver, yields a flocculent precipitate, which is likewise the case with salts of mercury and lead. The silver salt detonates when heated. The silver was determined in it several times as chloride; the results always differed. The reactions of this body agree with those described by Gerhardt.

By the action of manganese and sulphuric acid upon brucine, a substance was obtained in the aqueous distillate, which possessed a peculiar odour and reduced nitrate of silver in the form of a very beautiful mirror; it was not altered by potash, and was consequently no aldehyde; nor could any formic acid be detected in it.

From the foregoing experiments, although imperfect, it is evident that the gas evolved in the action of nitric acid upon brucine is not pure nitrous æther, and also that the formula of cacotheline cannot be that proposed by Laurent, although with respect to the amount of carbon and hydrogen the analyses agree.—Liebig's *Annalen*, Jan. 1848.

On the Action of Alkalies upon the Resin of the Root of Meum athamanticum, *and on the Presence of Mannite in this Root. By* H. Reinsch.

The author has succeeded, by treating this root with alcohol, evaporating, separating the resin, removing the last traces of the extract by æther, and redissolving the residue in alcohol of 0·868, in obtaining a large quantity of acicular crystals; they were collected on a filter, and washed with cold alcohol, and dissolved in boiling alcohol; the filtered solution deposited on cooling some brilliant needles, and the whole liquid finally congealed to a paste of crystals. After drying, these crystals were white, brilliant, of a sweetish taste, and presented all the characters of mannite. This substance appears to be more widely distributed in the vegetable kingdom than hitherto supposed, and it probably occurs in most of the roots of the *Umbelliferæ*.

The resin, which was soft and of a light brown colour, was first washed with cold water until it ceased to impart a yellow colour to it; it was then melted in boiling water, deprived of water as much as possible, and placed in contact with some dry caustic potash. A brown liquid formed, which was kept boiling for a long time in a retort, when it disengaged a small quantity of ammonia and an essential oil of a peculiar odour distilled over, of a slightly yellowish colour and lighter than water. After saturating the ammoniacal water with sulphuric acid, the oil assumed the odour of lemon. The potash-compound of the resin was dissolved in water, and saturated with a slight excess of sulphuric acid; this addition separated the

whole of the resin in grayish-yellow agglutinated flakes, and the liquid acquired the odour of valerian; on distillation, a slightly acid water with the odour of cinnamon passed over. The resin, freed from acid and sulphate of potash by washing, was submitted to dry distillation; it gave off a very volatile and yellowish oil, forming at least one-third of the resin, then a yellowish-green, opaline, denser oil, and in the retort remained a brittle black resin. At all events this resin appears to be distinct; its combination with potash is crystalline; it affords an ætherial compound on solution in absolute alcohol and treatment with gaseous hydrochloric acid. Sulphuric acid turns the resin brown, and when alcohol is poured into this solution, an odour of punch is given off.—*Jahrb. für Prakt. Pharm.*, xiv. p. 388.

Observations on the Nitrate of Magnesia and the so-called "Alcoholates." *By* P. Einbrodt.

It is generally admitted that some salts are capable of forming crystals in which alcohol acts the part of water of crystallization. According to Professor Graham*, it is requisite for their formation that the salt and the alcohol be perfectly anhydrous; he employed alcohol of 0·976 spec. grav. Such combinations are conceivable with salts that can be obtained anhydrous, such as chloride of calcium, nitrate of lime, &c.; but it is scarcely possible to imagine how, under the stated conditions, an alcoholate of the nitrate of magnesia can be formed. This salt cannot be obtained in the anhydrous state; its crystals with 6 atoms of water scarcely dissolve, according to Graham, in absolute alcohol, and not at all according to John; and yet, from a solution of the hydrated salt in alcohol not entirely deprived of water, crystals are said to be obtained which contain 73·2 per cent. absolute alcohol to 26·8 of the hypothetically dry salt! Admitting in these crystals absolute alcohol as replacing the water of crystallization, is to suppose that the alcohol in which $MgO\,NO^5\,6\,aq$ is dissolved, deprives the salt of the whole of its water; and notwithstanding another portion of the same alcohol is at the same time entirely deprived of water. The other hypothesis, that spirit, a mixed liquid, replaces the water of crystallization in the crystals, is equally inadmissible.

These considerations did not strike me when preparing two years ago the alcoholate of the nitrate of magnesia, for the purpose of exhibiting this class of compounds. I expected that the crystals obtained, the form of which was not further noticed, would part with alcohol on being heated; the nitric acid however was decomposed by the gentlest heat. Recently I had occasion to repeat the experiment; the result this time was totally different. At the bottom of the vessel in which the preparation was preserved, a yellowish stratum of a concentrated aqueous solution had collected; the crystals had sunk together, and each one now consisted of a fascicle of delicate needles. Some of these fascicles, which had been dried a couple of days previously between blotting-paper, and which

* Philosophical Magazine for October 1828.

had since continued dry, were used for the experiment. When heated they fused quickly, without the acid being decomposed; the fused salt was boiled for some time before this decomposition ensued; the vapours had not the least odour of alcohol. The crystals were consequently no longer an alcoholate; but I could not regard this compound of nitrate of magnesia as the ordinary salt with 6 atoms of water, as this, according to Berzelius, absorbs moisture from the atmosphere more rapidly than any other salt. I took 11·1624 grms. of the salt, dried as carefully as possible between blotting-paper, and heated it very gently in a weighed retort until red vapours were perceptible. Weighed when cold, the retort with the salt had lost 3·81 grms. in weight. The liquid which had collected in the recipient could not be ignited, was not very acid to the taste, but slightly reddened blue litmus-paper. It proved to be water, and distinctly showed the reactions of the acids of nitrogen. The water, on evaporation upon platinum foil, left a slight trace of magnesia, which had been carried over with the vapours. The residuary salt was now heated until the evolution of red vapours entirely ceased. There remained

	1·7900	MgO
which require (MgO = 257·752 NO^5 = 675).....	4·6876	NO^5
and.....	4·6848	HO
	11·1624	

There remained consequently of the alcoholate the ordinary hydrate with 6 atoms of water, for NO^5 has the same equivalent as 6HO. However, the salt exhibited some new properties, if the older statements are admitted to be correct.

The *ordinary salt*, MgO NO^5 + 6 aq, crystallizes in four-sided *rhombic* columns with oblique or truncated summits (Ure). It deliquesces in the air more rapidly than any other salt (Berzelius), slowly (Ure); parts at the fusing-point of lead with 5 atoms of water; the monohydrated salt can be obtained in the fused state at this temperature without experiencing decomposition (Graham).

The *salt obtained from the alcoholate* crystallizes in needles, which, observed under the microscope, form very long parallelopipeds with *accurate quadratic* bases. The salt only deliquesces *in a very moist* atmosphere. A couple of ounces, kept in my laboratory, had not deliquesced in two years. On evaporation of the fused salt, it distinctly parts with a portion of its acid below the fusing-point of lead *before the fifth atom of water* is expelled. $4{\cdot}6848 \times \frac{5}{6} = 3{\cdot}904$; red vapours were perceptible, and acid had passed into the receiver, when the loss in weight amounted only to 3·81. On continuing the evaporation, the quantity of aqueous vapour disengaged decreased, while the acid vapours increased.

I do not think the salt examined was an allotropic modification of the ordinary salt, but rather that the previous statements respecting its properties are inaccurate. The monohydrated salt is more than problematical. In Graham's paper (translated in the Annalen der Pharmacie, vol. xxix.) the quantity of water given in 27·12 salt is

evidently a mistake of print. If the number 6·17 be altered to 11·21 or 11·61, we obtain for the crystallized salt very nearly 6 atoms of water; and referring the loss in weight of this salt on fusion to this corrected amount of water, it is evident that Graham's residuary salt contained *more* water than corresponds to 1 atom. Nor does a dimorphism of the salt obtain. M. Czernay, who is very expert in microscopical observations, convinced me that regular quadratic columns separate from every solution of nitrate of magnesia, which subsequently adhere by their longitudinal axes; and these agglomerated masses of crystals appear to the naked eye as rhombic columns.

But to revert to our subject. I have endeavoured to show that it is impossible for an alcoholate of the nitrate of magnesia to be formed, if we imagine this compound to consist of dry salt and absolute alcohol. To judge from its change on keeping, it appears from the beginning to be nothing more than a tissue of minute crystals of the ordinary salt with 6 atoms of water which has imbibed a solution of the salt in alcohol; this drains off in the course of time, and allows the alcohol to evaporate.

Respecting the alcoholates in general, we possess too few data to form any opinion respecting their constitution; the following circumstances, however, appear to me worthy of attention. All the five salts which Graham obtained combined with alcohol, viz. chloride of calcium, chloride of manganese, chloride of zinc, nitrate of lime and nitrate of magnesia, are hygroscopic to a greater or less extent; moreover, the alcohol which Graham employed was not anhydrous. May not this small amount of water have been essentially requisite for the preparation of these alcoholates? If in all cases it depends on the fact of delicate crystals of the hydrate being first formed, all the alcoholates will have an analogous composition to that of the nitrate of magnesia, and as mere mixtures cease to form a class of anomalous compounds. Their very composition, as found by Graham, speaks against their existence. He found in the alcoholate of—

	per cent. of alcohol,				
$CaCl$.....	59·0	leading to the formula	$4CaCl$	$+ 7C^4H^6O^2$	
$MnCl$	47·9	...	...	$4MnCl$	$+ 5$ ...
$ZnCl$.....	15·0	...	...	$4ZnCl$	$+ 1$ ...
$CaONO^5$ ..	41·5	...	...	$4CaONO^5$	$+ 5$ ...
$MgONO^5$ ..	73·2	..	...	$2MgONO^5$	$+ 9$ ...

These formulæ scarcely bear the stamp of probability.—Liebig's *Annalen*, Jan. 1848.

Action of Potash upon Amber. By G. Reich.

When powdered amber is heated to boiling in a retort with a very concentrated aqueous solution of caustic potash, and distilled to dryness, a strong odour of camphor is disengaged, and the receiver contains an aqueous liquid, together with a white substance which possesses all the properties of camphor (stearoptene). This substance must however not be confounded with the succinic camphor

of M. Vogel, which is obtained by the destructive distillation of amber, and which has absolutely nothing in common with camphor, as it does not dissolve in water nor in alcohol, and very sparingly in æther.—*Archiv der Pharm.*, li. p. 26.

PATENT.

Patent granted to Paul Gilbert Prelier, *for Improvements in the Manufacture of dry Sulphuric Acid and Nordhausen Sulphuric Acid.*

The patentee commences his specification, by stating that, in consequence of the great affinity of sulphuric acid for water, it is difficult to concentrate the acid even to 66° B.; therefore, in order to obtain dry sulphuric acid, he combines simple sulphates with a fresh proportion of acid for the purpose of forming bisulphates, which he decomposes by the action of heat, and thus obtains dry sulphuric acid. The manufacture of dry acid naturally leads to the production of smoking or Nordhausen sulphuric acid, as the latter is formed by the addition of dry acid to sulphuric acid which has been concentrated to 66°, the specific gravity of the Nordhausen acid increasing with the quantity of dry acid added.

In carrying out the invention, the patentee prefers to employ 100 parts sulphate of soda, 2 parts sulphate of potash, and 2 parts sulphate of lime; but these proportions may be varied; and even if sulphate of soda alone be employed, dry sulphuric acid will be obtained. The mixture is put into freestone retorts, set in a suitable furnace; then, by means of a bent glass tube, the acid is introduced into the retorts, and heat is gradually applied. Shortly after the application of heat drops of water will proceed from the retorts, then acidulated water, followed by acid at 40°, 50° and 66°, and finally by acid which fumes or smokes. To enable the operator to judge correctly as to the progress of the operation, vessels containing water are placed to receive the drops of acid; and when each drop produces a sound resembling that which would result if a red-hot iron was immersed in the water, the acid that produces the noise is dry acid. Vessels to receive the acid are now placed below the retorts, and luted with clay; and the retorts are subjected to a strong heat until the acid ceases to drop into the vessels. Dry acid is thus obtained; but if it be desired to obtain Nordhausen sulphuric acid, a quantity of acid, concentrated to 66°, must be introduced into the receiving vessels, when they are placed below the retorts; and by the admission of the dry acid the density of the acid in the receiver will be increased to 67°, 68° and 69°, according to the quantity of dry acid that enters the receiver. By this means sulphuric acid is obtained perfectly clear, and never coloured like the Nordhausen sulphuric acid, nor charged with earth or other foreign matters.—Sealed June 29, 1847.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Volatile Products resulting from the Decomposition of Albumen, Fibrine, Caseine and Gelatine by Oxidizing Agents. *By* Dr. G. GUCKELBERGER.

THE author has submitted albumen, fibrine, caseine and gelatine to the oxidizing influence of mixtures of sulphuric acid with chromic acid and with manganese, and minutely examined the products of decomposition which are formed. We first proceed to notice the author's experiments upon caseine. The caseine employed for the investigation was obtained by allowing skimmed milk to curdle, and freeing it from the whey by washing and pressure; after this treatment it was conveyed into a solution of carbonate of soda heated to between 140° and 176°, and the solution thus formed kept for several hours at that temperature. The scum which had formed in this time was then removed, and the slightly turbid liquid precipitated with dilute sulphuric acid. The precipitate was repeatedly washed with water until the latter passed off clear on pressure. A sample of this caseine contained mere traces of fat, and was consequently not treated with æther and alcohol. The dry caseine was mixed in the proportions given below, first with sulphuric acid and manganese, and afterwards with chromate of potash and sulphuric acid, and the mixtures submitted to distillation. The distillate which forms the subject of this investigation contained, on decomposing the caseine with manganese and sulphuric acid—

1. Aldehyde of acetic acid ..... $C^5 H^3 O, HO$
2. Aldehyde of metacetonic acid?.. $C^6 H^5 O, HO$
3. Aldehyde of butyric acid ..... $C^8 H^7 O, HO$
4. Oil of bitter almonds..... $C^{14} H^5 O^2, H$
5. Formic acid ..... $C^2 H O^3, HO$
6. Acetic acid..... $C^4 H^3 O^3, HO$
7. Metacetonic acid ..... $C^6 H^5 O^3, HO$
8. Butyric acid ..... $C^8 H^7 O^3, HO$
9. Valerianic acid ..... $C^{10} H^9 O^3, HO$
10. Caproic acid ..... $C^{12} H^{11} O^3, HO$
11. Benzoic acid ..... $C^{14} H^5 O^3, HO$

And on decomposing caseine with chromate of potash and sulphuric acid—

1.	Aldehyde of metacetonic acid?	$C^6 H^5 O, HO$
2.	Oil of bitter almonds (in small quantity)	$C^{14} H^5 O^2, H$
3.	Formic acid (in small quantity)	$C^2 H O^3, HO$
4.	Acetic acid	$C^4 H^3 O^3, HO$
5.	Butyric acid	$C^8 H^7 O^3, HO$
6.	Valerianic acid	$C^{10} H^9 O^3, HO$
7.	Benzoic acid, with traces of caproic acid?	
8.	Benzoic acid	$C^{14} H^5 O^3, HO$
9.	Prussic acid	$C^2 N, H$
10.	Valeronitrile	$C^{10} H^9 N$
11.	A heavy oil, with the odour of cinnamon	
12.	Metacetonic acid	$C^6 H^5 O^3, HO$

We now proceed to give the evidence which the author brings forward in support of the above statements.

Treatment of Caseine with Manganese and Sulphuric Acid.—4½ parts of monohydrated sulphuric acid are diluted with twice the weight of water; and as soon as the mixture has cooled down to between 104° and 122°, 1 part of finely-powdered caseine added to it under constant agitation; in the course of a few hours the whole has dissolved. The solution, according to the temperature of the sulphuric acid, has a violet or a brown colour. It is set aside for a day, the fat which floats on the surface removed, a quantity of water added, the liquid mixed with 3 parts of manganese in a retort, and so much water added that for each part of caseine there are 30 parts of water. It was found to be advantageous not to use the whole of the manganese at once, but to begin the distillation with half the quantity mentioned, and to proceed with it as long as the distillate was worth collecting; and then to mix the remaining half of the manganese in the retort with a suitable quantity of water, and to recommence the distillation with the residue. Care must be taken to cool well.

Properties of the Distillate.—The liquid which passes over in distilling caseine with manganese and sulphuric acid till above one-half has been removed, possesses an acrid odour, which excites coughing and tears. Subsequently it becomes milder, and towards the end is replaced by that of prussic acid. In the nearly colourless and clear distillate a few white flakes are suspended.

The Volatile Acids.—The crude distillate is saturated with chalk, and one-half distilled from the perfectly-neutral liquid, which is now evaporated, the lime separated by means of carbonate of soda, and the soda salts subsequently decomposed with sulphuric acid. Butyric and valerianic acids were immediately perceptible from the odour.

The Neutral Products were contained in the distillate from the solution of the lime salts; it was perfectly neutral, but soon became acid by exposure to the air, and behaved towards reagents, towards potash and solution of silver, like a solution of aldehyde. This liquid was concentrated by repeated distillation, when a milky liquid was obtained, upon the surface of which a yellow oil, of an extremely penetrating odour, floated. After separation of this upper stratum

of oil, a heavy oil subsided from the water, which then became clear. This latter oil is converted with access of air into white crystals.

Separation of the Neutral Products.—The yellow oil was poured into a flask, provided with an ascending tube for the vapours, in order that the less volatile products might flow back again. The flask was heated in a water-bath at first to 104°; the liquid began to boil, and disengaged vapours, which condensed to a very mobile liquid, which mixed with water in every proportion, and possessed the suffocating odour of the original mixture in the highest degree. When the temperature of the water-bath had risen to 122°, and the liquid in the flask had ceased to boil, the recipient was changed and the temperature increased. Between 149° and 158° the contents of the retort again began to boil; the first portions which passed over still possessed the suffocating odour of the previous distillate; those which followed had an agreeable ætherial odour. Two strata had now formed in the flask; the lower one, amounting to somewhat more than a third, was water; the upper one, a yellow oil. At the boiling-point of water, a colourless oil passed over, which was sparingly soluble in water, and smelt like acetone. When nothing further passed over, on using the water-bath, a descending tube was employed, and the distillation carried on over a naked fire. The first portions contained some of the preceding distillate; the receivers were continually changed until the drops which passed over sunk after condensation to the bottom of the water which accompanied them.

Aldehyde of Acetic Acid, $C^4 H^4 O^2$, is contained in the product first removed. It was left in contact for several hours with chloride of calcium, and then distilled from a water-bath at a temperature which just sufficed to keep the liquid boiling. The receiver and the refrigerator were cooled with ice; the boiling-point could not be accurately determined; it was situated between 73° and 82°. The specific gravity at 59° was 0·0796; it formed a colourless liquid, which rapidly acquired an acid reaction by exposure to the air. The reactions to which the author submitted it agree with those of aldehyde. He also prepared aldehyde-ammonia from it, which was analysed. It afforded, on combustion with oxide of copper, and in one determination of the ammonia with chloride of platinum, after it had been decomposed with muriatic acid,—

	I.	II.	III.	IV.	H=1.		
Carbon	39·35	39·40	..	..	4=24		39·35
Hydrogen	11·30	11·50	..	..	7	7	11·47
Nitrogen	..	..	22·60	22·86	1	14	22·95
Oxygen	..	..	..	..	2	16	26·24

Aldehyde of Metacetonic Acid?, $C^6 H^6 O^2$, one of the substances contained in the second product, which distilled over between 149° and 158°, and was purified with great difficulty. It was several times rectified after drying over chloride of calcium; it boils in this state already at 104°. At first that which passed over between 131° and 140° was collected, but no constant boiling-point could be obtained

with this portion. The product had an agreeable ætherial odour, and a specific gravity of 0·79 at 59°; mixed with water in every proportion, and became slowly acid by exposure to the air, but rapidly in contact with platinum-black. It did not reduce a solution of silver. Of the portions which passed over subsequently and at a higher temperature, one was analysed which boiled between 140° and 149°; it was certainly mixed with a small quantity of a foreign substance, as caustic potash coloured it yellow, which was not the case with the preceding; in other respects the one could not be distinguished from the other. The analyses I. and II. were made with the first, III. and IV. with the latter substance:—

	I.	II.	III.	IV.	II=1.	
Carbon	61·96	61·84	62·03	62·33	3=18	62·06
Hydrogen	10·42	10·37	10·48	10·79	3	3	10·34
Oxygen	27·62	27·79	27·29	26·88	1	8	27·60

The density of the vapour of this liquid was found to be 2·169. Admitting that 1 equiv. of the substance contains 4 volumes of vapour, we have—

			Calculated.	Found.
6 vols. carbon	= 4·9920			
12 vols. hydrogen	= 0·8316	8·0422	= 2·0105	2·169
2 vols. oxygen	2·2186	4		
	8·0422			

The formula $C^6 H^6 O^2$ would correspond to the aldehyde of metacetonic acid, but perhaps also to the hydrate of metacetone; however, it was impossible to examine the properties of the substance more minutely, on account of the small quantity.

Aldehyde of Butyric Acid, $2(C^4 H^4 O)$, is contained in the third portion of the products of distillation. This substance is very sparingly soluble in water, and can be separated from the mixture by the addition of water; it boils at 154°–158°; its specific gravity is 0·8 at 59°. It dissolves in every proportion in alcohol and æther, is neutral, but quickly becomes acid on exposure to the air. It resembles in taste acetic aldehyde, behaves like it to ammonia and potash, reduces silver from solution in the form of a metallic mirror, and affords with concentrated sulphuric acid a blood-red liquid, without any separation of carbon being perceptible even on the application of heat. It afforded on combustion—

Carbon.....	66·14	66·40	4 = 24	66·66
Hydrogen	11·22	11·22	4	4	11·11
Oxygen	22·67	22·42	1	8	22·23

Butyric Aldehyde-Ammonia, $NH^3, C^8 H^7 O, HO + 10HO$.—When the preceding aldehyde is mixed with a dilute aqueous solution of ammonia, this substance separates in white crystalline crusts, which are insoluble in water, especially in water containing ammonia. The crystals are washed with ammoniacal water, and dried over lime in an atmosphere of ammonia. Acute rhombic octohedrons are perceptible with the lens. If the substance, after solution in strong alcohol, is allowed to crystallize by the slow evaporation of the sol-

vent, it is obtained in tolerably large tables, the acute angles of which are truncated. Water separates the compound from its solution in alcohol. It dissolves in æther. Once dried, the crystals are permanent in dry air; but if exposed to the air while moist or to a humid atmosphere, they soon acquire an empyreumatic odour and a brown colour; they behave therefore, in this respect, quite similarly to aldehyde-ammonia. When heated, this compound melts, and the vapours are precipitated on the cold sides of the vessel in the form of limpid drops, which subsequently solidify to a crystalline mass. Only towards the end of the experiment was a minute quantity of ammonia disengaged. When heated rapidly it is decomposed; caustic potash does not eliminate the ammonia. When acids are added to it, they deprive the compound of ammonia and separate the original substance unaltered. On analysis the ammonia compound afforded—

Carbon	26·74	26·64	..	..	8	=48	26·81
Hydrogen	11·84	11·90	..	..	21	21	11·73
Nitrogen	..	..	7·69	7·94	1	14	7·82
Oxygen	..	..	..	..	12	96	53·64

A quantity of the compound was now decomposed by diffusing it in water and distilling it with a solution of alum. Upon the distilled water floated a colourless liquid, which after drying over chloride of calcium was the body $C^8 H^8 O^2$ or $C^8 H^7 O, HO$ in a state of perfect purity. It gave on analysis 66·43 carbon, 11·23 hydrogen, and 22·54 oxygen; and consequently leaves no doubt respecting the formula above given for the butyric aldehyde-ammonia.

This aldehyde immediately affords butyric acid in contact with the air, and also when mixed with readily-reducible metallic oxides. On placing a quantity of it over water, in a beaker under a bell-glass filled with air, the substance had become completely acid in the course of a few days; it was saturated with soda, the soda salt precipitated with a solution of silver, and the silver salt burnt. The analysis gave the following results, which agree with those of the butyrate of silver:—

Carbon	24·32	8	48	24·61
Hydrogen	3·80	7	7	3·58
Oxygen	16·32	4	32	16·43
Silver	55·56	1	108	55·38

On boiling the substance with oxide of silver, butyrate of silver was likewise formed with separation of metallic silver. It also appears that this aldehyde affords with sulphuretted hydrogen a base resembling thialdine. The butyral described by Chancel* is perhaps an isomeric body. This butyral was also obtained by Henneberg, according to the method described by Chancel, *i. e.* by distilling the butyrate of lime; but from the statements which exist respecting butyral, it cannot be stated with certainty in what relation it stands to this aldehyde. We must therefore not yet consider butyral and

* Chem. Gaz., vol. iii. p. 54.

the substance proved by the author to be really butyric aldehyde to be identical, although Chancel regarded butyral as the aldehyde of butyric acid.

Oil of Bitter Almonds.—Among those products not possessed of acid properties, which were separated by interrupted distillation from one another, was a liquid which finally passed over on distillation over a naked fire. It was heavier than water, possessed the odour of oil of bitter almonds, and the property of becoming solid by contact with the air. The crude product was left for twelve hours with chloride of calcium, the clear portion decanted and distilled. The liquid boiled at 338°; the boiling-point then rose rapidly to 356°, where it remained a long time stationary; the greater portion was distilled over between 356° and 361°; the specific gravity of the product was 1·038 at 59°, and in other respects it possessed all the properties of oil of bitter almonds. The solid substance into which the distillate was converted exhibited all the characters of benzoic acid; and the following analysis proved beyond all doubt that the first body is in fact oil of bitter almonds, and the latter benzoic acid:—

	Oil of Bitter Almonds.				Benzoic Acid.			
Carbon.....	79·23	14=84		79·24	68·39	14=84		68·85
Hydrogen....	5·85	6	6	5·66	5·02	6	6	4·91
Oxygen.....	15·52	2	16	15·10	26·59	4	32	26·24
	100·00		106	100·00	100·00		122	100·00

The silver salt was moreover found to contain 50·95 per cent. oxide of silver; the formula of the benzoate of silver requires 50·55.

The Acids.—It was stated above that the acids were in the first place combined with lime, the lime salts decomposed with carbonate of soda, and upon this the volatile free acids obtained by decomposing the soda salts with sulphuric acid and distilling. On concentrating the solution of the soda salts, an abundant crop of crystals of acetate of soda separated. The mother-ley contained a salt insoluble in alcohol, which separated on further evaporation in tabular crystals. It was separated from acetate of soda by treatment with alcohol. The acid of this salt exhibited all the properties of formic acid, which was moreover confirmed by an analysis of the lead salt.

On purifying this formiate of soda, the author noticed the existence of a formiate of soda with 6 atoms of water of crystallization. A solution, evaporated at the ordinary temperature of the room, deposited some slender silky needles, which deliquesced in the air and effloresced over sulphuric acid. Dried between blotting-paper, the salt contained 45 per cent. of water, corresponding to the formula of a salt with 6 atoms of water, which requires 44·18 per cent. As soon as no more crystals formed on further evaporation of the mother-ley separated from the acetate and formiate of soda, it was mixed with twice its volume of dilute sulphuric acid, consisting of 1 part concentrated acid to 2 of water. The mixture was set aside for a day, in which time the sulphate of soda crystallized out; above

the crystals was an aqueous liquid, and upon this floated a tolerable quantity of a brownish oil, which was carefully removed with a pipette, and shaken several times with an equal volume of pure water, to separate the more readily soluble butyric acid from the valerianic acid, which were distinctly recognised by their odour. The wash-water, and the aqueous liquid above the crystals of sulphate of soda, were united, saturated with carbonate of soda, and then evaporated to dryness in a water-bath. The dried mass was now again decomposed with sulphuric acid of the same strength, and thus a layer of a nearly colourless oil obtained; this oily acid began to boil at a few degrees above 212°, but the boiling-point only exhibited some constancy at 266°; what passed over at that temperature and at 284° was collected separately; lastly, a small quantity of an acid was obtained, the boiling-point of which was between 320° and 329°.

Metacetonic Acid.—The liquid which passed over between 266° and 284° contained metacetonic acid; it did not mix in every proportion with water; after neutralization with ammonia and the addition of nitrate of silver, a granular precipitate of a silver salt fell, which was decomposed for the greater part at the boiling temperature of water; but a portion again separated on the cooling of the solution. The crystals became black in the water-bath, fused at a higher temperature, and were decomposed with evolution of acid vapours. The boiling-point of metacetonic acid is situated, according to Gottlieb, at 284°. The acid under consideration, obtained between 266° and 284°, has all the known properties of metacetonic acid. An estimation of the silver in the silver salt afforded 59·30 per cent. silver; the formula $C^6 H^5 AgO^4$ requires 59·66.

According to Gottlieb's observations, metacetonate of silver forms a double salt with the acetate of silver. To prepare this salt, the liquid from which the metacetonic acid had been obtained, and the boiling-point of which was situated at 266°, was saturated with ammonia, and nitrate of silver added to the boiling liquid. An abundant separation of reduced silver took place, probably owing to the presence of formic acid. From the filtered boiling liquid, shining, white, dendritic crystals separated on cooling, which became black in the water-bath, and did not fuse at a higher temperature. On analysis, the relation between the carbon and hydrogen was found to be as 5 to 4, and that of the silver to the carbon as 2 to 10, or precisely the relations which correspond to the salt described by Gottlieb*. The mixture from which the metacetonic acid was obtained proved consequently to be a mixture of formic acid, acetic acid and water.

Butyric Acid.—It has been previously stated that, besides the metacetonic acid, a small quantity of a liquid was obtained, the boiling-point of which was situated between 320° and 329°. This liquid is perfectly colourless. As butyric acid boils at 327°, it was possible that this liquid might be butyric acid; it was consequently burnt with oxide of copper, and afforded the following numbers,

* Chem. Gaz., vol. iii. p. 158.

which agree very closely with the per-centage composition of butyric acid :—

Carbon	54·02	8 =	48	54·54
Hydrogen.....	9·33	8	8	9·09
Oxygen	36·65	4	32	36·37
	100·00		88	100·00

Caproic Acid.—The brownish oil, of which it was observed above that it possessed the odour of valerianic acid, was likewise distilled; a nearly colourless liquid passed over, which had the offensive odour of the fatty acids. Towards the end of the operation a white crystalline substance coated the neck of the retort, which increased in quantity until the contents of the retort were quite dry and carbonized. This substance was collected by means of æther and subsequent evaporation; on examination it proved to be benzoic acid. The oily distillate was mixed with the liquid which remained after the separation of the butyric and metacetonic acids, and had a boiling-point above 329°. On saturating this mixture with barytic water, three different salts were obtained on crystallization, of which the first that separated was caproate of baryta. The quantity of the salt was too small for many experiments to be made with it. It was anhydrous, and consisted of hemispherical aggregations of small prisms. Its amount of baryta was found to be 41·30. The formula of caproate of baryta requires 41·72.

Valerianic Acid.—Immediately after removing the preceding salt, nacreous laminæ of valerianate of baryta separated from the mother-ley. On the addition of nitrate of silver to the solution of this baryta salt, caseous flakes separated, which dissolved in water on boiling, and subsequently separated in laminæ resembling the acetate of silver. The baryta salt contained no water of crystallization. The following numbers contain the results of the analysis :—

Carbon	28·83	10 =	60	28·70
Hydrogen	4·41	9	9	4·30
Oxygen	..	4	32	15·33
Silver	51·79	1	108	51·67
			209	100·00

The third salt crystallized in anhydrous transparent groups of prisms, which dissolved in water with great ease, separating only when the solutions had attained a syrupy consistence. In this property it agrees with the butyrate of baryta, which is confirmed by analysis, for on combustion it afforded—

Carbon	30·59	8 =	48·0	30·84
Hydrogen	4·63	7	7·0	4·49
Oxygen	15·59	3	24·0	15·45
Baryta	49·19	1	76·6	49·22
	100·00		155·6	100·00

Besides these three salts was a fourth, which separated in the form of a powder at the same time as the caproate of baryta, and

appeared to be somewhat less soluble than the latter salt. From the small quantity it was impossible to examine it further.

Products of Decomposition of Caseine by Chromic Acid.—When caseine is distilled with bichromate of potash and sulphuric acid, the liquid which passes over has different properties to that obtained in the distillation with manganese and sulphuric acid; it has a very powerful odour of prussic acid, and tastes of cherry-laurel, is rendered turbid by white flakes floating in it, and has an acid reaction. To obtain this product, the best proportions are 3 parts of sulphuric acid, 30 parts water, and 2 parts bichromate of potash; in this instance the caseine is first dissolved in the sulphuric acid diluted with 2 parts of water, and then added to the solution of the bichromate in 10 parts of water. The reaction, which immediately begins with great violence, is moderated by adding the remaining quantity of water; the distillation then goes on quietly. Reagents showed the presence of a considerable quantity of prussic acid in the distillate and the total absence of aldehydes. The prussic acid was removed by rectification over peroxide of mercury; yet the distillate still contained a substance which imparted an odour of prussic acid to it; it was saturated with lime, and again distilled, when it afforded a turbid aqueous liquid, upon which floated a colourless oil. By rectifying the aqueous liquid separated from the oil, a further quantity of oil was obtained, and it then lost the odour of prussic acid. From the small quantity of the aqueous milky portion of the distillate, an oil with the odour of cinnamon and a burning spicy taste subsided. It is evident that, after separating the prussic acid by peroxide of mercury, the other acids, as in the treatment with manganese, remain combined with lime in the residue of the retort. We may therefore again consider the several bodies as neutral and acid products.

The Neutral Substances.—As above stated, an oil with the odour of cinnamon separated from the mixture; and, owing to its high specific gravity, collected below the water of the distillate. The author obtained too little of this body to examine it more minutely; it did not solidify by exposure to the air, and is not oil of bitter almonds. The oils which floated upon the water were separated into a nitrogenous and a non-nitrogenous body.

The non-nitrogenous substance is the aldehyde of metacetonic acid (?) $C^6 H^6 O^2$. It is difficult to separate from the nitrogenous substance, and was obtained only in small quantity from the portions passing over between 158° and 248°, and rectifying the products until a liquid was obtained which boiled between 131° and 140°. The author describes the physical properties, and gives the results of two analyses, which all agree with what has been above enumerated. A determination of the density of the vapour gave 2·069, which, assuming 4 vols. of vapour to 1 equiv. of the compound, comes very near to the calculated number, 2·0105.

The Nitrogenous Substance (valeronitrile) forms the greater portion of the distillate which boiled between 248° and 284°. It was obtained pure by repeated distillation, rejecting the first and last portions which passed over. Its boiling-point fluctuated between

257° and 262°; its specific gravity at 59° was 0·813; its odour resembled that of oil of bitter almonds, and its taste was aromatic, bitter and burning. In other respects, it was colourless, very liquid, soluble in about 4 times its volume of water, and mixing in every proportion with alcohol and æther; it burnt with a white flame without any smoke. The numbers enumerated below show that the substance agrees in its composition as well as in its properties with the body obtained by Schlieper in the decomposition of gelatine by chromic acid *, and to which he gave the name of valeronitrile. The analysis gave—

	I.	II.	III.			
Carbon.....	71·81	71·90	..	10	=60	72·28
Hydrogen.....	10·83	10·94	..	9	9	10·84
Nitrogen	..	..	16·79	1	14	16·86

The specific gravity of the vapour was found to be 2·892; theory gives 2·877; moreover, on distilling this valeronitrile with the addition of some sulphuric acid, valerianic acid was obtained. Schlieper has shown that valeronitrile is disposed by acids and alkalies to assimilate 3 equivs. water, and thus to become converted into ammonia and valerianic acid.

In the liquid remaining from the preparation of the valeronitrile which boiled above 262°, there was found, after it had been distilled to a very small quantity, a small amount of a substance which solidified by exposure to the air, and then proved to be benzoic acid.

The Acid Products.—The solution of the lime salts of the acids, the prussic acid having already been removed by peroxide of mercury, were treated as previously described, with the exception of the immediate separation of the benzoic acid. On adding an acid to the solution, which had been concentrated to a syrup, crystals of benzoic acid immediately separated. The author then prepared from the distilled filtrate, formic, acetic, valerianic and butyric acids; the latter probably contained some metacetonic acid.

The action of the chromic acid differs from that of the manganese by the appearance of prussic acid and valeronitrile; otherwise the results are very closely related. The prussic acid and the valeronitrile may be looked upon as ammonia salts of formic and valerianic acids, in which 3 equivs. water have been eliminated; and, in fact, these two acids are found, but in small quantities, among the products obtained with bichromate of potash; they are, as it were, replaced by the above salts, which have been produced by a higher temperature than that employed in the treatment with manganese. This indeed explains why the residue, after treatment with manganese, gives off so large a quantity of ammonia with lime, that one would almost imagine the whole of the nitrogen of the caseine had passed off in the form of ammonia, while mere traces are eliminated from what remains after treatment with chromic acid. Moreover, the manganese mixture, according to the proportions above given, contains an excess of sulphuric acid, which fixes the eliminated am-

* Chem. Gaz., vol. v. p. 10.

monia, while in the mixture of chromate of potash the sulphuric acid is almost perfectly neutralized by the potash. Schlieper observed, that in order to obtain valeronitrile from gelatine, a certain amount of sulphuric acid must not be exceeded, as otherwise only acids are found in the product; a fact which the author's experiments confirm. It remains then to show in what manner the ammonia salts of formic and valerianic acids can lose water. According to Döbereiner's observations, formiate of ammonia is decomposed already at 356° into prussic acid and water. An analogy for the origin of valeronitrile occurs in the production of benzonitrile; according to Fehling, benzoate of ammonia passes at a high temperature into benzonitrile. In this connexion the prussic acid appears as formyl-nitrile, $C^2HO^3, NH^3 - H^3O^3 = C^2NH$, just as the expression $C^{14}H^5O^3, NH^3 - H^3O^3$ leads to $C^{14}H^5N$ benzonitrile. It may certainly be admitted that the mixture of sulphuric acid and chromate have so high a boiling-point that the decomposition of the valerianate of ammonia into valeronitrile and water, and also that of the formiate of ammonia into prussic acid and water, obtains; and thus the appearance of these products of decomposition in the place of the acids themselves which are obtained in the treatment with manganese, depends solely on the temperature and quantity of oxidizing agent, but not on the amount of sulphuric acid. If, finally, in the treatment with chromic acid, the aldehydes of acetic and butyric acids are not among the products, this is owing to the amount of oxygen in the mixture being sufficient to oxidize them. Perhaps the excess of sulphuric acid required from the nature of the manganese, renders the appearance of valeronitrile impossible.

[To be continued.]

On the Presence of Ammonia in the Atmosphere.

By Geo. Kemp, M.D. Cantab., F.C.P.S.*

The existence of ammonia in the atmosphere has been long suspected as a source from which the vegetable world derives a portion of the nitrogen detected by analysis in all such parts as are destined to perform functions accessory and essential to life. Analogical reasoning and indirect experiment, as conducted both by Saussure and Liebig, seem to have established the point, that rain and snow contain ammonia, under circumstances which ensured its exclusion from any other source than the atmosphere; it must, however, be obvious to the cautious experimentalist, that difficulties of no ordinary magnitude attach themselves to the determination of an almost inappreciable quantity of a substance from one incomparably greater, submitted to a variety of operations, every one of which presents a source of error, whilst many of the details were necessarily conducted by the inferiors of a laboratory, who could not be presumed capable, either morally or physically, of exercising the full amount of caution necessary in manipulations of so delicate a nature.

* Communicated by the Author.

The *Société Hollandaise*, considering the subject as undecided, proposed a renewal of the investigation in terms which are thus given in the 'Chemical Gazette' for 1846, p. 423.

"The opinion that the nitrogen contained in the various organs of plants owes its origin to the ammonia which is diffused in the atmosphere, is gaining ground every day. This view is opposed to all that is known respecting the nature of the atmosphere and its influence on the nutrition of vegetables, and not a single argument exists placing it beyond all doubt. The Society requires that the proofs for and against this view be discussed, and that the quantities of nitrogen contained in plants be determined by fresh investigations."

The writer of this paper had long contemplated making some experiments on the subject, and trusts that the following brief summary may be of service, the more especially as the results of the successful candidate for the prize are not yet known.

In order to determine the point in question satisfactorily, it seemed desirable to simplify the conditions, and consequently diminish the sources of error as much as possible; and, to do this, it was necessary to operate directly on the atmospheric air in an isolated uncombined state, and to select a locality for observation in which the adventitious presence of ammonia, from manure and other matters, could not reasonably be suspected. After some preliminary trials, the following methods were adopted:—

A glass vessel was selected, capable of holding half an imperial gallon, or about 138 cubic inches, which was closed by a cork pierced with three holes, in which were inserted respectively a glass siphon, the shorter arm reaching to the bottom of the vessel, a glass tube funnel reaching also to the bottom, and a glass tube bent at right angles; the free extremity of the last was furnished with a caoutchouc connecting-tube, which united the whole with the second division of the apparatus. This consisted of a wide mouth flask, capable of holding 6 fluid ounces, furnished with a cork pierced with two holes, into one of which was inserted a tube bent at right angles, one extremity being united with the tube before mentioned, and, like it, extending at the other extremity just below the surface of the cork; the other aperture received a straight glass tube reaching to the bottom of the smaller flask. These arrangements completed, before fixing the corks in position, the larger flask was filled with water, the smaller, to the depth of a quarter of an inch, with a strong but not saturated solution of bichloride of mercury in water. The corks were now introduced, and, in order to ensure their being air-tight, were covered with a varnish of melted caoutchouc. The place selected was a hill, about 300 feet above the level of the Irish Sea, long. 5° 30′, lat. 34° 12′, in which the accidental presence of ammonia was not at all likely to affect the result.

Having placed the whole apparatus on a stand 4 feet from the ground, the siphon was set in action, and a current of air was consequently passed through the solution of bichloride of mercury; the

larger flask, when emptied, was again supplied with water, and the operation being several times repeated, a distinct turbidness was observed in the solution contained in the smaller flask. Thus encouraged to proceed, it was determined to make an arrangement by which the current of air might continue for a much longer period without intermission; and for the water-flask was substituted a reservoir capable of holding 2760 cubic inches. The following are the notes entered at the time:—

"*April 30th*, 1847.—Engaged in determining whether ammonia is contained in the atmosphere. Yesterday 10 gallons of air, passed through a solution of corrosive sublimate, produced a hardly appreciable precipitate. To-day a violent hail-storm, with rain, came on at 11½ A.M.; and, on proceeding to the examination of the solution, I was surprised to find a most distinct precipitate, though certainly not more than 2 gallons could have run off, that is to say, of the water displaced by the air. This ammonia then would appear to have been generated during or after the storm; had the ammonia already existed diffused through the atmosphere, it must have been returned to the earth by the rain, which could not pass into my apparatus."

Circumstances prevented the immediate repetition of the experiment, which was subsequently made in a different locality, a few miles southward, and at an elevation of about 50 feet above the sea, the results of which are thus noted:—

"*June 30th*, 1847.—Apparatus of the same kind as above, but the reservoir capable of holding 12,420 cubic inches, which permitted the experiment to go on continuously for twelve hours, commencing at 11 A.M., temperature at midday 82° F. in the sun, B. 30·55. A beautiful day, hardly a cloud visible. Concluded the experiment at 11 P.M. The quantity of amide so small that I determined not to separate the precipitate, but leave it in the solution."

"*July 1st.*—11 A.M. continued the experiment, having refilled the reservoir. Temperature at noon 92° F. At 11 P.M. the precipitate was found increased in apparently the same proportion. Ammonia in the 24,840 cubic inches amounting to 1·8 milligrm."

As the chloro-amidide of mercury is an inconvenient form for the determination of ammonia, in consequence of the extreme fineness of the precipitate, it was converted by boiling into HgCl + 2HgO + HgAd. This precipitate may be separated by filtration with great ease and rapidity; and, on account of the high atomic weight of the compound, is a valuable agent for the determination of minute quantities of ammonia. By substituting a solution of corrosive sublimate for the chloride of platinum in the determination of nitrogen by Will's method, the whole of the tedious process of evaporation is saved; and, in bodies rich in nitrogen, the danger of the hydrochloric acid being drawn into the combustion-tube by sudden absorption is avoided.

From the above experiments it seems fair to conclude that the presence of ammonia in the atmosphere is established, and that the

quantity is considerably greater than analogy would lead us to expect*.

Ellenbrook, Isle of Man, Feb. 16, 1848.

On the Specific Gravity of Selenium. *By* Count SCHAFFGOTSCH.

Fused selenium solidifies, when quickly cooled, to a glassy mass of conchoidal fracture; when slowly cooled, on the contrary, it becomes granular and presents an uneven fracture. This well-known peculiarity rendered it probable that these two different conditions would equally correspond to different specific gravities, a supposition which has been confirmed by very numerous experiments.

The investigation extended to selenium in pieces as well as in powder, and had to overcome two great difficulties, which, if they had not been obviated, would have yielded too low a specific weight. It is very difficult to obtain pieces of selenium which do not inclose air-bubbles; and the selenium in powder, from its weak adhesion to water, can only be imbued with this liquid by the constant use of the air-pump; a complete moistening, consequently a complete removal of the air from the powder, could not even be obtained by boiling with water; it could however be more easily moistened with alcohol, on which account in many cases spirit was used instead of water, the density of which had been accurately ascertained. The specific gravity of the vitreous selenium was found to be at 68° F., 4·276–4·286, the mean of which is 4·282.

To prepare the granular selenium, from 8 to 12 grms. were heated in a mass of sand up to 482° F., and after being kept for an hour at this temperature, allowed to cool. Selenium thus treated, on being moderately magnified, presented very evidently the structure of glass slag at some places, and yielded upon porcelain a less red streak than the vitreous. Its specific gravity at 68° was found to be 4·796 to 4·805; on an average therefore 4·801, which is to the average of the vitreous selenium as 112·1 to 100. It is still undecided whether a still slower cooling would produce a higher specific gravity.

The blood-red selenium, as it is obtained for instance on the reduction of selenious acid with sulphurous acid, possesses the property of becoming grayish-black at a moderate heat, and apparently diminishing considerably in bulk. The specific gravities of the red and gray precipitates were determined, and the number 4·259 found for the red at 68° and 4·264 for the gray. Consequently the specific gravity of the red precipitate corresponds to that of the vitreous selenium, and is not altered by becoming black, for the differences are such as may be ascribed to an error of experiment.—*Bericht der Berl. Acad.*, Nov. 1847.

* At a period subsequent to the above experiments, the writer met with a notice of the "Determination of the Amount of Ammonia contained in the Atmosphere," by A. Græger, in the 'Chemical Gazette,' vol. iv. p. 34, and is happy that the oversight has been the means of confirming M. Græger's researches in the most independent manner.

On Hydrocyanharmaline, a new Base. By Dr. FRITZSCHE.

Harmaline enters into a very remarkable combination with prussic acid. It is not, as usual, a salt that is produced by the union of the prussic acid with the alkaloid, but a new base, which combines with other acids to form salts without any prussic acid being eliminated. Nor is the harmaline separated from the hydrocyanharmaline by alkalies. The salts which it forms are very distinct from those of harmaline, and it is quite certain that hydrocyanharmaline is a new alkaloid, formed by the conjugation of prussic acid and harmaline. Both bodies combine directly, and also on the double decomposition of soluble cyanides with salts of harmaline; free prussic acid even converts the harmaline in the acetate into hydrocyanharmaline. Of the different methods which may be employed to prepare the new base, the following yields the most favourable result:—A dilute boiling alcoholic solution of prussic acid is saturated with harmaline, and filtered hot; on cooling, the new alkaloid separates in small rhombic tables. Large quantities of hydrocyanharmaline may be very quickly procured by adding the solution of a salt of harmaline to one of cyanide of potassium in water, or, instead of the cyanide of potassium, to a solution of prussic acid, and then adding the alkali. As hydrocyanharmaline is insoluble in water, it separates immediately in the form of a flocculent white precipitate, which even under the microscope appears amorphous, and on drying is partially decomposed with evolution of prussic acid. This decomposition is avoided by dissolving the precipitate, while still moist, in hot alcohol, when, upon cooling, crystals of the compound separate; or an alcoholic solution of harmaline can be employed, when the precipitate is obtained in the form of a crystalline powder. Any admixture of harmaline can be removed from the hydrocyanharmaline with a little acetic acid, as this readily dissolves the former, and acts but slightly upon the latter.

The new base forms in the pure state thin rhombic tables, which are not altered by exposure to the air nor at 212°, but at about 356° are entirely decomposed into prussic acid and harmaline. Likewise on boiling with water, in which it is insoluble at the ordinary temperature, and with spirit, in which it dissolves more at a higher than at the ordinary temperature, it gradually experiences the same decomposition.

Composition of Hydrocyanharmaline.—On the union of prussic acid with harmaline no water is absorbed, nor is any water eliminated upon its decomposition into its two proximate constituents. Analysis moreover shows that it is composed of equivalent proportions of harmaline and prussic acid; it was submitted to an elementary analysis, and the weight of the constituents determined in a weighed quantity. The combustion gave—

Carbon.....	69·89	29	2178·48	70·481
Hydrogen	6·49	15	187·20	6·057
Nitrogen	..	3	525·18	16·991
Oxygen	..	2	200·00	6·471

On heating hydrocyanharmaline in a bath of chloride of zinc, and passing over it a current of dry air, the whole of the prussic acid was expelled and the harmaline left unaltered; the results were—

Harmaline	89·04	1	2753·08	89·072
Prussic acid	10·96	1	337·78	10·928

Hydrocyanharmaline saturates exactly the same quantity of acid as the harmaline contained in it would saturate; but all its salts are less stable, and have a very great tendency to separate into prussic acid and salts of harmaline. Similar decomposition results partially even before and after the separation of the salts of hydrocyanharmaline from the solutions of the alkaloid in acids, and the more readily the more dilute the solutions are. Even the salts themselves are decomposed on drying in the same manner, and also in the course of time into salts of harmaline and prussic acid, the odour of which they consequently diffuse. In their decomposition they pass from the colourless state into a yellowish-coloured one. It is consequently difficult to prepare such salts sufficiently pure for analysis, and as yet the composition of the muriate has alone been ascertained. In preparing the salts, the ready-formed hydrocyanharmaline is dissolved in the acids. It appears that compounds cannot be obtained with all acids, for instance not with acetic acid. Likewise when salts of harmaline (except the acetate) are mixed with prussic acid, salts of hydrocyanharmaline are not formed.

Muriate of Hydrocyanharmaline.—When hydrocyanharmaline is first mixed with some water and then with muriatic acid, the whole dissolves, and subsequently the muriate separates in the form of a powder, consisting of minute, well-defined crystals; they are rhombic octohedra, with secondary surfaces, and are readily distinguished by means of the microscope from the long prisms of the muriate of harmaline. If quickly removed from the mother-ley, they are obtained free from muriate of harmaline and sufficiently pure for analysis. In one analysis the salt was boiled with water, the expelled prussic acid passed into a solution of nitrate of silver, the residuary solution of muriate of harmaline decomposed by ammonia, the precipitated harmaline determined, and afterwards the muriatic acid by a solution of silver. The numbers obtained are compared with those calculated:—

Harmaline	77·63	1 =	2753·08	77·625
Prussic acid	9·51	1	337·78	9·524
Muriatic acid.....	12·86	1	455·76	12·851

Sulphate of Hydrocyanharmaline is obtained by adding sulphuric acid to the harmaline, when various phænomena are observed according to the concentration of the acid. The most concentrated acid dissolves the alkaloid, without any decomposition, to a yellow liquid, which, both by the spontaneous attraction of water or by the careful addition of the latter, becomes colourless, and deposits crystals of the sulphate of hydrocyanharmaline. A somewhat diluted acid converts the alkaloid, with apparent retention of its form and without any previous perceptible solution, into the sulphate; if, on

the contrary, the alkaloid is mixed, in the state of a fine powder, with sufficiently diluted acid, the whole dissolves at first to a clear and colourless liquid, from which, after some time, a portion of the salt separates in compact microscopic crystals, which can no more be confounded with those of the sulphate of harmaline than the preceding salt with the muriate.

Nitrate of Hydrocyanharmaline.—When hydrocyanharmaline is mixed with nitric acid, an oily body, floating in the mother-ley, is first produced from the union of the two bodies, which subsequently solidifies to a crystalline mass. If the alkaloid is mixed up in a finely divided state with much water, it dissolves on the addition of nitric acid to a clear liquid, which after some time deposits crystals of the nitrate, but usually also of the nitrate of harmaline.

Constitution of Hydrocyanharmaline.—Fritzsche adopts Berzelius's view concerning the constitution of the alkaloids, regarding them as bodies conjoined with ammonia. According to this, harmaline = $C^{27}H^{14}N^2O^2$, consists of ammonia and the conjunct $C^{27}H^{11}NO^2$. This latter body has entered into combination with prussic acid, and the salt thus formed has again united with the ammonia to form a conjugated compound. In this respect hydrocyanharmaline is related to those bodies in which the conjunct is a nitrite of an organic oxide. The easy assimilation and elimination of the prussic acid in the composition of harmaline, throws more light upon the nature of the conjugated bodies than any other of this class of compounds hitherto known. The following rational formulæ are therefore proposed for hydrocyanharmaline and its compounds:—Hydrocyanharmaline-ammonia

$$= h\,c\,y\,h\,m\,l\,Ak = (C^{27}H^{11}NO^2 + CyH) + Ak.$$

Hydrocyanharmaline and chloride of ammonium

$$= h\,c\,y\,h\,m\,l,\,AmCl = [(C^{27}H^{11}NO^2 + CyH) + Am]\,Cl.$$

Sulphate of hydrocyanharmaline and oxide of ammonium

$$= h\,c\,y\,h\,m\,l,\,AmO,\,SO^3 = [(C^{27}H^{11}NO^2 + CyH) + AmO]\,SO^3.$$

Metamorphoses of Hydrocyanharmaline.—The author merely notices a few facts respecting the behaviour of hydrocyanharmaline, which tend to throw more light on the nature of this body. Oxidizing agents do not act upon it as if it were a prussiate of harmaline, but give rise to peculiar products of decomposition. When finely-divided hydrocyanharmaline is suspended in water and mixed with a large excess of nitric acid, and this mixture heated to boiling, while the greater portion of the alkaloid dissolves, the liquid soon assumes a beautiful purple colour, with evolution of nitrous acid, and when filtered while hot, deposits on cooling a brilliant red powder, which appears under the microscope to consist of round amorphous granules. The filtered mother-ley deposits a further quantity of this body on dilution with water, which is likewise the case when it is nearly saturated with ammonia; but an excess of ammonia precipitates a beautiful green body, into which the red body is immediately converted in contact with ammonia. This red body is not

very stable; it dissolves in alcohol pretty easily with a beautiful purple colour; but this soon passes into a dirty yellow one, and it is not possible to reobtain the red body unaltered by evaporation of the red solution. Æther does not assume a red colour, but it extracts a substance which is left on evaporation, and of which it has still to be ascertained whether it is an admixture or a product of metamorphosis. When nothing more is precipitated by water, the liquid still contains other substances; moreover, the products of decomposition vary when the method is modified, or when, instead of water and nitric acid, alcohol and nitric acid are employed. Muriatic acid and chlorate of potash convert hydrocyanharmaline into a resinous body.—*Bulletin de St. Pétersburg*, vi. p. 290.

ANALYTICAL CHEMISTRY.

On a new Method of distinguishing the Protoxide of Iron from the Peroxide by the Blowpipe. *By* Edward J. Chapman, Esq.*

The presence of iron in any compound may be detected, it is well known, and with great certainty, by the blowpipe; but no method has hitherto been given by which the protoxide of iron can be distinguished from the peroxide by means of that instrument. After several trials to accomplish this, I discovered the following method, which is both decisive and simple, requiring moreover for its performance but the ordinary reagents of the blowpipe-case.

A very minute quantity of oxide of copper is to be dissolved in a bead of borax on the platinum wire until the glass be faintly coloured; and the substance under examination being added to it, the whole is to be subjected, but for an instant only, to a reducing flame; when, if protoxide of iron were originally present in the assay-matter, the CuO will be reduced to Cu^2O, forming small red spots or streaks, which become visible as the glass cools. The FeO is converted into Fe^2O^3 at the expense of the oxygen of the copper.

In the above experiment, if the glass were exposed for too long a time, the oxide of copper might become reduced, even if the substance under examination contained only the peroxide of iron, as this would be converted by the flame into protoxide, and thus act, as before stated, on the oxide of copper; and if, furthermore, this latter substance were contained in too large a quantity in the borax glass, it might become reduced by the sole action of the yellow flame, and thus give rise to an erroneous result. To obviate, therefore, all doubt as to the presence or absence of FeO in any compound, I find it advisable to conduct the operation in a different manner, by which not the slightest uncertainty can be experienced.

The borax bead must be coloured by a sufficient quantity of oxide of copper to render it of a fine blue tint, but transparent, when cold.

* Communicated by the Author.

To this the substance under examination in powder must be added, and the bead exposed for a moment, or until the iron compound begins to dissolve, to an oxidating flame. If peroxide of iron alone be present, the glass will remain transparent, and of a green or bluish-green colour; but, on the contrary, if the added substance contained protoxide of iron, the glass on cooling will be marked with opake red patches, due to the reduction of the CuO to Cu^2O, as before explained. Care must be taken not to continue the blast too long, otherwise the suboxide of copper might be again oxidized, and the whole of the protoxide of iron converted into peroxide. After one or two trials, however, no error can possibly arise.

This reaction is not prevented by the presence of silica or other acids. Amongst the silicates, the *hedenbergite* (a variety of *augite*) $3CaO, 2SiO^3 + 3FeO, 2SiO^3$, the dark-coloured *hornblendes* $\left.\begin{matrix}CaO\\MgO\end{matrix}\right\} SiO^3 + 3FeO, 2SiO^3$, *lievrite* $3(3\frac{CaO}{FeO}SiO^3) + 2(Fe^2O^3, SiO^3)$, and other minerals, give very positive results.

Finally, it will be perceived that in certain cases the protoxide of iron, either alone or in combination as a salt, may serve to replace tin in the detection of oxide of copper by the blowpipe. For instance, when testing for minute portions of copper with borax on the platinum wire, the glass must be removed to a piece of charcoal if we wish to render evident the red suboxide by means of tin; for otherwise the end of the wire would be destroyed, the tin forming with it a fusible alloy. By employing, however, a small fragment of sulphate of iron to ensure this reduction, the bead may still be retained on the platinum wire; and we shall thus effect a saving of time and trouble, and preserve our charcoal for other experiments, an advantage of no little consequence when travelling, or in situations where good charcoal is not easily procurable. Nevertheless, it must be confessed, that, under other circumstances, tin is, for this purpose, the better reagent of the two.

On a Method of detecting the Presence of Sulphate of Cinchonine in the Sulphate of Quinine, and of estimating its Amount. By O. Henri.

Having been requested to analyse several samples of sulphate of quinine from various sources, with a view to detect any sulphate of cinchonine, supposed to exist in them to a considerable amount, I had occasion to make various experiments, the publication of which may prove useful.

As is well known, cinchonine always accompanies quinine in the barks. Although its medical properties have a certain analogy with those of quinine, they do not possess the same energy; and, moreover, as the proportions of sulphate of cinchonine mixed with that of quinine are variable, and as I have had occasion to find, frequently very considerable, the sulphate of quinine can no longer possess the same intensity in its medical action nor the same constancy in its effects. In the preparation on a large scale of the sulphate of qui-

nine; that of cinchonine, being far more soluble, remains in the mother-ley, and mere traces can adhere to the former. Now when we find sulphate of cinchonine, to the amount of 4, 6, 8, 10, 15, &c. per cent., there can be no doubt that it has been added fraudulently.

To detect the presence of sulphate of cinchonine in sulphate of quinine, I first tried the processes proposed by Mr. Calvert and by M. Oppermann*. The first of these processes consists in adding to a saturated solution of the suspected sulphate of quinine a solution of chloride of lime (hypochlorite). The sulphate of quinine gives at first a white precipitate, but the deposit dissolves in an excess of the reagent; whilst the sulphate of cinchonine yields, *according to the author*, an abundant precipitate, which is permanent. In the second process, that of M. Oppermann, a suitable amount of sulphate of quinine is dissolved in tartaric acid; it is diluted with from 200 to 300 parts of pure water, and an excess of bicarbonate of potash or soda added. Under the influence of the tartaric acid, M. Oppermann states that the quinine does not yield any precipitate, whilst the other base gives an abundant deposit.

I have several times repeated these two processes, and must confess that I found them totally deficient in accuracy; for in the first the chloride of lime, whilst forming with the sulphate of cinchonine a more apparent precipitate, did not the less dissolve the whole when added in sufficient excess. With respect to the second, the bicarbonates of potash and soda equally furnished abundant precipitates, which were formed more or less slowly in the tartaric solutions. Sometimes I obtained no precipitate either in one or the other salt. The want of success which I experienced induced me to follow a different method, which, although requiring more time, leads, when *carefully* made, to very good results, according to experiments which I have made upon mixtures of sulphates of quinine and cinchonine in the proportions of 2, 4, 10 and 15 per cent. of the latter.

From 20 to 30 grms. of the sulphate of quinine to be examined are dissolved in a certain quantity of distilled water slightly acidulated, and an excess of caustic soda added to the solution. The collected and washed precipitate is saturated with hot acetic acid; the mixture solidifies on cooling to a crystalline mass, which is thrown upon a filter of fine linen and expressed; the clear solution, evaporated to one half, yields on cooling more crystals, which are separated in the same manner. The mother-water is then decomposed again with dilute caustic soda, and the precipitate formed is, after washing, treated in the cold either by æther or by alcohol of 0·923. After this treatment, it is boiled twice, or more frequently, in absolute alcohol, and filtered boiling hot. The alcoholic solution, evaporated with care and to dryness, leaves the cinchonine in minute acicular crystals, which can be weighed. This method, which it is true is somewhat tedious, is successful with mixtures containing only 2 per cent. I obtained very satisfactory and closely approximative results.—*Journ. de Pharm.*, Feb. 1848.

* Chem. Gaz., vol. iii. p. 477.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Platino-cyanides. *By* B. QUADRAT.

THE *Platino-cyanide of Potassium*, which is obtained according to Gmelin's method by heating prussiate of potash and spongy platinum to redness, has the formula $PtKCy^2 + 3HO$, advanced for it by Gmelin and Rammelsberg. But when protochloride of platinum, obtained by igniting the perchloride, is mixed with cyanide of potassium, the yellow iridescent crystals obtained on evaporation possess a different composition to Gmelin's salt. On boiling with sulphuric acid, protocyanide of platinum is precipitated, which on solution in cyanide of potassium again forms the same salt. It is likewise obtained from perchloride of platinum and cyanide of potassium. It still retains 1·95 per cent. of water at 212°; altogether the salt contains 15·98 per cent. water of crystallization or 21 atoms, of which 14·03 per cent. or 18 atoms escape at 212°. In the analysis, the results of which, reduced to anhydrous substance, are related below, the platinum was determined by decomposing the salt with sulphuric acid, heating to redness, and washing out the sulphate of potash, while the cyanogen and the amount of water of the salt dried at 212° were calculated from the amount of carbon and hydrogen found by elementary analysis. This salt afforded—

Platinum.....	48·77	47·89	48·49	5	=6165·0	48·63
Potassium	23·12	23·26	..	6	2933·4	23·18
Cyanogen.....	27·69	..	..	11	3575·0	28·19

It crystallizes in long, slender, four-sided prisms, which appear yellow by transmitted light and blue by reflected (Gmelin's salt is more of a greenish tint). It soon effloresces in the air, and gradually becomes rose-coloured, which even takes place after the salt has been previously dried at 212°. It dissolves in alcohol and æther, but not so readily as in water. On boiling with concentrated sulphuric acid, yellow protocyanide of platinum is eliminated, still containing some sulphate of potash, which cannot be removed by washing. It affords with proto- and persalts of mercury white precipitates. With the first reagent, if an excess of it be employed, a small blue precipitate is obtained. 1 part of the salt dissolves in 3 parts by weight of water at 61°.

Platino-cyanide of Sodium, $Na^6 Pt^5 Cy^{11} + 28HO$.—The solution

of the preceding salt affords with dilute solutions of sulphate of copper a precipitate of platino-cyanide of copper, which is insoluble in acids. On boiling this precipitate with carbonate of soda, the copper is removed, and the liquid contains platino-cyanide of sodium, which separates in large crystals on evaporation. It is best to use an excess of the copper precipitate, as the salt is then obtained more readily pure from carbonate of soda. It forms large colourless crystals, which are isomorphous with those of carbonate of soda. At 212° it loses 19·35 per cent. or 21 atoms of water, and at 248° 2·21 per cent. or 7 atoms more. Its reactions agree with those of the preceding salt. On analysis the salt afforded—

Platinum	53·72	5 =	6165	53·68
Sodium	14·76	6	1747	15·18
Cyanogen	31·52	11	3575	31·14

Platino-cyanide of Ammonium, $(NH^4)^6\,Pt^5\,Cy^{11}$ at 212°, is very readily obtained by mixing the platino-cyanide of potassium with sulphate of ammonia. It is evaporated to dryness, and the residue exhausted with alcohol, which dissolves the salt, leaving behind sulphate of potash and ammonia. On evaporating the alcoholic solution, slender acicular crystals of a lemon-colour are obtained, which have a strong diamond lustre, with lavender, violet and rose-coloured tints. The crystals are very soluble in water, become brown on desiccation without experiencing any decomposition, and afford a colourless solution. The following results agree most with the formula above adopted. The ammonia and cyanogen were calculated from the hydrogen and carbon obtained on combustion:—

Platinum	56·21	5 =	6165	55·6
Ammonium	11·68	6	1350	12·2
Cyanogen	32·11	11	3575	32·2

Platino-cyanide of Barium, $Ba^6\,Pt^5\,Cy^{11} + 22HO$, is prepared in the same manner as the sodium compound, using caustic baryta instead of soda. The excess of baryta is removed by carbonic acid, and the solution evaporated, when the salt separates in permanent crystals 2 lines in length and ½ a line in breadth. According to Hauer, they are rhombic prisms. The lateral surfaces have a splendid blue iridescence, are pale yellow, and appear in certain directions by transmitted light green. 1 part of the salt dissolves in 33 parts water at 61°. When heated, it first becomes white, then brownish. At 212° the salt parts with 7·73 per cent. or 12 atoms of water, and at 284° it again loses 6·98 per cent. or 10 atoms. The analysis gave—

Platinum	41·1	5 =	6165·0	41·4
Barium	34·5	6	5128·8	34·5
Cyanogen	24·4	11	3575·0	24·1

The strontia compound may be obtained in the same manner as the preceding salt.

Platino-cyanide of Calcium, $Ca^6\,Pt^5\,Cy^{11} + 27HO$, is prepared with caustic lime in the same manner as the preceding salt; it forms

yellowish-green scales, which are easily soluble in water, and when heated up to 212° part with the whole of their water, first becoming rose-red, then reddish-white, and lastly perfectly white. It contains 20·44 per cent. or 27 atoms of water of crystallization. To determine the platinum, the salt was burnt with an addition of nitric acid; the lime was determined as oxalate, and the cyanogen by the loss. It gave—

Platinum	54·7	5	54·8
Calcium	13·0	6	13·4
Cyanogen	32·3	11	31·8

Platino-cyanide of Magnesium, (I) $Mg^6\ Pt^5\ Cy^{11} + 19HO$, is obtained by decomposing the platino-cyanide of barium with sulphate of magnesia, evaporating to dryness after removing the sulphate of baryta and exhausting the residue with alcohol, which dissolves the salt, leaving sulphate of magnesia behind. Very perfect crystals are obtained on slowly driving off the alcohol. It is still more easily prepared by mixing solutions of the potassium compound and sulphate of magnesia, evaporating to dryness, and exhausting the residue with a mixture of æther and alcohol. On evaporating the solution, the salt separates in crystals. They are quadratic prisms; the groups of crystals exhibit a beautiful play of colours, being carmine-red in transmitted light, with green and blue metallic colours by reflected light. A few drops of the solution of the salt, evaporated to dryness upon a watch-glass, furnish a green coating with a metallic lustre, which appears red when seen through. At 95° the crystals become pale yellow without changing their form; at 212° of a white colour; when moistened, the surface again assumes a metallic lustre. They dissolve very readily in water, 1 part of the dry crystallized salt in 3·4 parts of water at 61°. At 212° the salt loses 18·69 per cent. or 11 atoms of water, but still contains in this state 8 atoms. The magnesia was determined as ammonio-phosphate of magnesia, the platinum by decomposing the salt with nitric acid and subsequent ignition, the cyanogen from the amount of carbon found by an elementary analysis. Calculated for the anhydrous salt, the results are—

Platinum	57·8	5	57·8
Magnesia	8·7	6	88·0
Cyanogen	33·2	11	33·4

Platino-cyanide of Aluminium is obtained by mixing a solution of sulphate of alumina with one of the platino-cyanide of potassium, and extracting the dry residue with strong alcohol. The salt can be obtained in a crystalline form from this solution. The crystals are yellow, deliquesce quickly, and assume a green colour at 212°; they become reddish-brown at a higher temperature, and burn like tinder.

Platino-cyanide of Copper, $Cu^6\ Pt^5\ Cy^{11}$, at 284° is precipitated, on the addition of a solution of a sulphate of copper to one of the platino-cyanide of potassium, in the form of a light green precipitate, which is insoluble in dilute nitric acid and in concentrated muriatic acid, may easily be washed, and turns dark green on drying. For

analysis, the salt dried at 284° was employed, decomposed by ignition with sulphuric acid, exhausted with boiling water, the platinum collected on a filter, and the cyanogen ascertained by the loss. It afforded—

Platinum	50·7	5 =	6165	50·8
Copper	19·4	6	2376	19·6
Cyanogen	29·9	11	3575	29·6

On digesting this salt with ammonia and evaporating the solution, blue acicular crystals were obtained, which are easily soluble in water, and likewise in alcohol and æther. By exposure to the air, they part with ammonia and water, and are again converted into platino-cyanide of copper. Acids separate unaltered platino-cyanide of copper. In the following analysis the cyanogen is determined from the amount of carbon found on combustion:—

Platinum	43·90	1 =	1233·0	43·75
Copper	13·55	1	396·0	14·06
Ammonia	14·31	2	455·0	15·08
Cyanogen	23·90	2	650·0	23·07
Water	4·56	1	112·5	4·04

Platino-cyanide of Mercury.—The platino-cyanide of potassium furnishes, with a solution of corrosive sublimate, a white precipitate, which is insoluble in water and in nitric acid, but dissolves to a clear liquid in muriatic acid. If a solution of the protonitrate of mercury, instead of the corrosive sublimate, be employed, on adding the first drops a white precipitate is formed, on further addition a yellow one, then a green, and finally a blue one. The blue substance is insoluble in water containing free nitric acid. In hot water the blue colour passes back again through green and yellow into white, and protonitrate of mercury can then be detected in the water. The same decomposition gradually occurs on washing it with cold water. The precipitate, which has been rendered white by washing, again acquires the blue colour on pouring some protonitrate of mercury over it. The white precipitate obtained from a solution of corrosive sublimate likewise becomes blue on the addition of protonitrate. However, these compounds could not be analysed quantitatively, as they were decomposed in the drying. According to certain reactions, however, the white precipitate would appear to have a similar composition to the potassium compound; the blue precipitate appears to be a combination of protonitrate of mercury with platino-cyanide of mercury.

Besides the salts above described, the following were obtained,—the *lead salt* as a yellowish-white precipitate; the *persalt of iron* in flesh-coloured flakes, which on drying become brown; and the *silver salt* in white flakes, which do not blacken by exposure to the light.

Platino-cyanic Acid, $PtHCy^2$, was obtained by decomposing the platino-cyanide of copper with sulphuretted hydrogen, in which reaction prussic acid is disengaged. The liquid filtered from the sulphate of copper is quickly evaporated to dryness, and the residue exhausted with a mixture of alcohol and æther. The acid crystal-

lizes in bluish-black prisms with a reddish-yellow metallic lustre, which contain water of crystallization; they very soon absorb moisture from the atmosphere, and deliquesce. The alcoholic solution leaves upon glass when heated a mirror of platinum. When an aqueous solution is mixed with nitric acid, long, colourless, acicular crystals are subsequently obtained. The acid becomes yellow at 212°, then reddish-yellow, and finally white; but even at 284° it experiences no decomposition. The platinum was determined by heating the acid with nitric acid, the hydrogen and carbon by combustion with oxide of copper:—

Platinum	65·04	1 =	1233·0	65·07
Hydrogen	0·62	1	12·5	0·63
Cyanogen	34·14	2	650·0	34·30

The acid absorbs ammonia, expels carbonic acid from the alkaline carbonates forming platino-cyanides, and is decomposed when heated with sulphuric acid into protocyanide of platinum and prussic acid.

Platino-cyanide of Magnesium, (II) $MgPtCy^2$.—By saturating platino-cyanic acid with carbonate of magnesia, the simple compound $PtMgCy^2$ was now likewise obtained; it has nearly the same appearance and crystalline form as the salt (I) above described. It is readily soluble in water. The crystals turn reddish-brown when heated to 212°. It still retains 12·19 per cent water of crystallization at 284°. The analysis of the salt gave, after deducting the amount of water determined by an elementary analysis—

Platinum	59·68	1 =	1233·0	60·40
Magnesium	8·03	1	157·7	7·74
Cyanogen	32·29	2	650·0	31·86

As in all these combinations the platinum cannot be detected by the usual reagents until they have been decomposed, the author admits the existence of a radical *platino-cyanogen* = Cpty. The compounds above described then obtain the following formulæ:—Platino-cyanic acid = Cpty + H; Gmelin's salt = Cpty . K; the magnesia salt II. = Cpty . Mg; the ammonia salt of copper = Cpty + Cu + $2NH^3$. The other salts above described are represented by the formula 5(Cpty + R) + CyR + xHO.—Liebig's *Annalen*, lxiii. p. 164.

On the Absorption of Carbonic Acid by Sulphuric Acid. *By* Prof. Rogers.

At the meeting of the Association of American Geologists and Naturalists, held at Boston in September last, Prof. W. B. Rogers gave an abstract of a series of experiments lately made by himself and Prof. R. D. Rogers, on the absorption of carbonic acid by different liquids. In these investigations, the important fact was ascertained, that sulphuric acid at 60° F. absorbs carbonic acid gas in the large proportion of 94 per cent., and that Nordhausen acid absorbs 125 per cent. Prof. Rogers pointed out how this fact must affect

the accuracy of certain methods of determining the amount of carbonic acid in the free atmosphere, as in the experiments of Boussingault and others, and of that contained in the air of mines and in the air expired in respiration. The use of the sulphuric acid as a drying agent in these processes, as well as in the apparatus of Fresenius for analysing the carbonates, was thus shown to be attended with serious errors, in consequence of the absorption of the carbonic acid by the desiccating agents.—*Ed. Monthly Journ.*, Feb. 1848.

On some Volatile Products resulting from the Decomposition of Albumen, Fibrine, Caseine and Gelatine by Oxidizing Agents. *By* Dr. G. GUCKELBERGER.

[Continued from page 99.]

Products of Oxidation of Albumen, Fibrine and Gelatine.—A comparison of what has been communicated respecting the products of decomposition of caseine by chromic acid, with Schlieper's observations on the products resulting from the action of chromic acid upon gelatine*, shows a great agreement between the bodies thus produced. We shall now proceed, in the first place, to notice the products of decomposition of albumen, gelatine and fibrine with manganese and sulphuric acid, and then those produced by the action of chromic acid.

The fibrine employed in these experiments was obtained by beating fresh blood; it was washed with cold water until the water ran off colourless, then washed a few times with hot water, pressed and dried. The albumen was likewise prepared from blood; the blood-corpuscles were separated by means of a saturated solution of sulphate of magnesia, and the albumen precipitated in the coagulated state by heating the still faintly red liquid. It was washed with hot water, pressed, and then dried. The gelatine employed was the best that could be procured in commerce. The plan of operation was precisely the same as described when treating of caseine.

Decomposition by Manganese and Sulphuric Acid.—The distillate obtained in the decomposition of the three substances by manganese and sulphuric acid exhibited no difference; they all contained not a trace of prussic acid, and presented the reactions of aldehydes and of free acids. The acids were saturated with lime, and the neutral products separated by distillation from the solution of the lime salts. As the mode of treatment is in general the same, we shall merely give the results. The neutral oily products were separated by distillation into four liquids of different boiling-points.

Acetic Aldehyde was again the principal substance of the first portion which passed over. A greater amount was obtained from gelatine than from albumen and fibrine. The analysis made by the author agreed perfectly with the per-centage calculation according to the formula $C^4 H^4 O^2$.

The Body $C^6 H^6 O^2$ (*Metacetonic Aldehyde*).—A sufficient quan-

* Chem. Gaz., vol. v. p. 9.

tity of this substance was obtained from fibrine and albumen; it is contained in that portion which boils between 122° and 176°. It was not obtained from gelatine. Either it is not formed from gelatine, or only in such small quantity that it cannot be separated from acetic and butyric aldehydes; and this is the sole difference which is observed between the products of decomposition of gelatine and those of albumen, fibrine and caseine.

Butyric Aldehyde.—Little of this substance, which passes over at the boiling-point of water, was obtained from gelatine and albumen, more from fibrine. After purification by repeated rectification, the product exhibited the characteristic behaviour above described towards a solution of ammonia.

Oil of Bitter Almonds.—The odour of the product, the property of passing into benzoic acid by exposure to the air, as well as the analytical results enumerated by the author, show that from all three substances this oil is formed as with caseine.

The Acids.—The same agreement which obtains between the neutral products of oxidation of albumen, fibrine and gelatine with those of caseine likewise occurs among the acids; acetic acid and formic acid were in all three substances most abundant relatively to the other acids; fibrine afforded most butyric acid; gelatine more valerianic acid than the other substances; benzoic acid was in all cases only present in small quantity. It was not possible to obtain the metacetonic acid pure or in combination with silver; but the first portion of acid which was obtained below 266°, in the purification of the butyric acid by distillation, and which must have contained the metacetonic acid, if any were present, together with acetic acid, yielded with oxide of silver a salt, which by solution in boiling water and recrystallization was obtained in the same form as the well-known double salt discovered by Gottlieb. Unfortunately, only one silver determination could be made; 61·71 per cent. silver were found; theory requires 62·06. No caproic acid was observed, but it was undoubtedly present, for the valerianic acid always possessed the disagreeable odour not peculiar to the pure acid, and the amount of silver always came out somewhat too low. Very considerable quantities of the substances must be operated upon, in order to detect the presence of caproic and metacetonic acids.

Treatment with Chromate of Potash and Sulphuric Acid.—In this instance the products from the albumen, fibrine, gelatine and caseine are again perfectly identical. The distillates are all rich in prussic acid. In all a small quantity of an oil, of the odour of cinnamon, separates after rectification over peroxide of mercury, and a large amount of acetic acid was contained in the acid products; more butyric acid was obtained from fibrine than from albumen and caseine. Valeronitrile, in perfect purity, was obtained both from albumen and fibrine. The non-nitrogenous substance, mentioned under caseine, could not be obtained in sufficient quantity to be purified.

The treatment with sulphuric acid and manganese, to which the author submitted caseine, gelatine, albumen and fibrine, as also that

of caseine, albumen and fibrine with chromic acid, proves, in conjunction with Schlieper's investigation of the products of decomposition of gelatine by chromic acid, that all these substances behave essentially in the same manner towards chromic acid or manganese and sulphuric acid. It must not however be thought that the products originate by a simple oxidation; the fact that a larger amount of volatile products is obtained when the solutions of the substances are allowed to remain for some length of time dissolved in sulphuric acid, shows that the sulphuric acid first gives rise to a separation into organic groups. Now since in the treatment with manganese and with chromic acid,—two substances which hold the oxygen with different affinity,—the products remain constant, it follows that these products are dependent only on a certain amount of oxygen, and not on the time in which this is absorbed. From the investigations of Bopp, several of the products into which these substances separate when treated with mineral acids are known, for instance, leucine and thyrosine. Again, we know that leucine separates, under certain circumstances, into ammonia and valerianic acid, both of which are constantly present among the products of decomposition which form the subject of this treatise. We are also able to point to the group from which the oil of bitter almonds takes its origin.

If the results above enumerated are not sufficient to explain satisfactorily the relation between the four substances, nevertheless it appears, from the relative quantities of the products of decomposition, that fibrine forms, as it were, the transition from caseine or from albumen to gelatine. In comparing quantitatively the several amounts of the products, it is impossible, in an investigation like this, to start from the absolute quantities of caseine, fibrine, &c. employed; but the oily mixture, as obtained after repeated rectification, affords for the non-volatile products a point from which to calculate the quantities of the several products of decomposition from a weighed amount of the crude oil. But the acids, which correspond to the substances contained in the oil, must likewise be taken into consideration, as it is evident that acetic aldehyde and acetic acid, oil of bitter almonds and benzoic acid, are derived from the same organic groups; they must therefore be taken together. Now if we arrange caseine, albumen, fibrine and gelatine according to the amount of acetic acid they afford on oxidation, they will follow in the order just enunciated. Gelatine afforded most acetic acid, and also the most formic acid. If they are arranged according to the quantities of benzoic acid and oil of bitter almonds they furnish, they will stand as follows,—gelatine, fibrine, albumen, caseine; the latter yielding the greatest amount. Fibrine is distinguished from all the others by the remarkably large amount of butyric acid and its aldehyde which it affords; gelatine gave the least, but most valerianic acid; the least amount of which was afforded by caseine and albumen.

The appearance of aldehyde among the products of decomposition of caseine and gelatine renders it probable that aldehydes are produced in the oxidation of the fats before the series of acids $(CH)^nO^4$

is formed. Aldehyde, which has hitherto been known only as a product of oxidation of alcohol, was likewise obtained by the author in treating milk-sugar with chromate of potash and sulphuric acid, and by Engelhardt in the distillation of lactate of copper. From this we might be led to suspect that the constituents of the blood enclose as a proximate constituent a non-nitrogenous body, a hydrocarbon, perhaps milk-sugar or fat, which affords the aldehyde on treatment with manganese and sulphuric acid.—Liebig's *Annalen*, lxiv. p. 39.

On Dammara Resin. By Dr. A. B. Dulk.

This resin has already been examined by Bils, Brandes and Dr. R. Thomson; the author has since submitted it to a more minute investigation. Dammara resin consists, according to him, of a hydrocarbon, which he calls dammaryle, which is most probably the original secretion of the plant, and of such products as may be deduced from it by oxidation and the assimilation of the elements of water.

The pulverized resin, inclosed in fine capillary tubes of glass, melted at 73° Cent. This melting-point would agree with that found by Thomson, who gives 165° C., if we admit that C. has been inserted by mistake for F. in his paper. The resin left 3·9 per cent. ash. Alcohol and æther removed but very little; concentrated sulphuric acid, sulphuric æther and fatty oils dissolved it entirely; other dilute acids dissolved for the greater part nothing. Nitric acid dissolves it, but decomposes it at the same time. Potash has but little action upon it, and ammonia still less. The powder dissolves in the cold in English sulphuric acid, according to the quantity of the acid, to a yellow or red liquid, which becomes black from the gradual progressive decomposition. If the sulphatic solution, in which all application of heat has been avoided, is poured into water, a greenish precipitate falls. The Dammara resin, dried at 122°, yielded, on the combustion of some very pure fragments, the following numbers:—

Carbon.....	82·65	82·66	82·46	82·37	82·53
Hydrogen ..	11·21	11·32	11·32	11·31	11·29
Oxygen	6·14	6·02	6·22	6·32	6·18

Products of Decomposition.—On boiling the pulverized resin for seven hours with chlorate of potash, it formed a white froth, although there was nothing organic dissolved in the water; the froth-like substance floating on the surface had absorbed 25·96–26·23 chlorine. On dry distillation, with six times its weight of soda-lime, for about twelve hours, at a temperature rising from 220° gradually to 608° F., hydrogen, and subsequently hydrocarbons, were given off. On separating the bases from the residue by muriatic acid, the resin appeared of a yellow colour. The aqueous liquid smelt decidedly of valerianic acid, but contained not a trace of oxalic acid. The yellow resin was perfectly neutral, and dissolved almost entirely in hot absolute alcohol, from which it again separated on cooling. This product, dried

at 212°, yielded on combustion 78·52 carbon, 10·45 hydrogen, and 11·03 oxygen.

Proximate Constituents of Dammara Resin.—On mixing pulverized Dammara resin with a very large quantity of alcohol of 0·863 spec. grav., it caked together. The spirit removed 74 per cent. Absolute alcohol subsequently dissolved out of the residue 5 per cent. more; the insoluble residue was now boiled with water, which extracted 0·1 per cent. of gum. That portion of the resin which remained after digestion with water was treated with æther, which dissolved 13·5 per cent., and left 0·2 mineral constituents and 7·2 insoluble residue. That which had been extracted by absolute alcohol and alcohol of 0·863 proved to be the same substance; the resin was consequently again treated with hot spirit of 0·901, which deposited a portion on cooling, but held a certain amount in solution; the insoluble residue was treated with absolute alcohol, the residue of the latter again with æther, which still left a residue. The resins obtained in this manner are,—1st, δ-resin, dammaryle = 13·5 per cent., soluble in æther; 2nd, α-resin = 24·5 per cent., dissolved by weak spirit, and not separating on cooling; 3rd, β-resin = 10·5 per cent., soluble in hot weak spirit, and separating on cooling 4th, γ-resin = 44 per cent., extracted with absolute alcohol; and 5th, the insoluble ε-resin = 7·5 per cent.

1. *Dammaryle*, $C^{46}H^{38}$.—It is obtained from the Dammara resin, which has been exhausted with absolute alcohol by treatment with æther. If precipitated from this solution with alcohol, it parts with something, for dammaryle is very readily oxidized, and the product of oxidation is taken up by the alcohol. After desiccation it forms a shining mass, which is easily pulverized; the powder is tasteless and not electrical; it melts when heated to a yellow glass, and gave on analysis—

Carbon	87·60	87·93	87·96	46	87·89
Hydrogen	12·05	12·07	12·44	38	12·10

Dammaryle absorbs oxygen when frequently exposed to the atmosphere. The analysis of a sample which was thus exposed, gave—

Carbon	86·16	85·96	46	85·71
Hydrogen	11·76	11·76	38	11·80
Oxygen	2·08	2·28	1	2·49

On keeping dammaryle for some time in steam heated up to 230°, it assumed the same composition as the natural Dammara resin, viz.—

		Natural Dammara resin.	
Carbon	82·45	82·5	82·5
Hydrogen	11·51	11·3	11·3
Oxygen	6·04	6·2	6·2

As this substance absorbs so readily the elements of water, it was treated with chlorine by heating it with chlorate of potash and muriatic acid. In the course of eight hours it absorbed 26·99 per cent., after sixteen hours 33·38 per cent., and after twenty-four hours' treatment 33·73 per cent. chlorine.

α-Resin, $C^{46}H^{39}O^{4}$, is that portion of the natural Dammara resin which remains dissolved in the cold weak spirit. In the course of several days it experienced, in a moist atmosphere of oxygen, no change either at the ordinary temperature or at 86°–95°. It affords a very electrical powder, is perfectly insoluble in water, and melts at 133°; the alcoholic solution of the resin reddens blue litmus; mixed with an alcoholic solution of potash, it affords no precipitate, but assumes a darker colour. It was attempted to prepare the metallic salts of the α-resin, but found impossible, however modified the method, to produce a constant compound. This resin is composed of—

Carbon	80·14	79·47	79·43	46	=3450	79·54
Hydrogen	10·86	10·79	10·72	39	487	11·22
Oxygen	9·00	9·74	10·87	4	400	10·24

The β-Resin is that which separates from the hot weak spirit on cooling. It has nearly the same properties as the former; its melting-point is situated between those of the resins α and γ. This β-resin is nothing more than a mixture of α- and the following γ-resin. The analysis afforded—

Carbon	80·01	80·38
Hydrogen	10·92	10·98
Oxygen	9·07	8·64

γ-Resin (*Dammarylic Acid*), $C^{46}H^{38}O^{3}$, is what remains dissolved in absolute alcohol after removal of the preceding by weak spirit. It melts at 140°, and dissolves in æther, sulphuric acid and oils. When rubbed, its powder becomes very electrical. It has a slight taste, a more acid reaction than the preceding resins, and melts in hot water, sinking to the bottom. If to the hot solution of this resin in absolute alcohol a solution of nitrate of silver, and afterwards an alcoholic solution of ammonia is added to it, a gelatinous precipitate falls, which was washed with cold alcohol and dried at 212°. From the alcohol employed in washing, a further quantity of the silver salt subsequently separated, which was washed first with alcohol and then with water. The substance, dried at 212°, was of a yellow colour, and appeared to be pure; on analysis it gave—

Carbon	69·54	46	69·57
Hydrogen	9·51	38	9·59
Oxygen	6·31	3	6·19
Oxide of silver	14·64	1	14·65

It is evident from this that the α-resin is a hydrate of the γ-resin, $C^{46}H^{39}O^{4} = C^{46}H^{38}O^{3} + HO$.

ε-Resin, $2(C^{46}H^{38}) + HO$.—The residue of the Dammara resin, which was insoluble in æther, and remained after all the preceding substances had been extracted, forms beneath the æther a doughy mass, which tenaciously retains some of the æther. When dry it forms a shining gray mass, which is easily reduced to powder, be-

comes soft at 400°, and melts at 419°. Hot oil of turpentine dissolves it; potash and ammonia are without action upon it; concentrated sulphuric acid most readily decomposes it. After the resin had been boiled with water to remove the last traces of æther, it was dried at 356° and burnt; it gave—

Carbon	86·49	86·58	92	86·66
Hydrogen	11·70	11·80	76	12·08
Oxygen	1·81	1·72	1	1·26

The author is of opinion that this last resin does not pre-exist in the Dammara resin, which consists rather of the hydrocarbon dammaryle and dammarylic acid. The expression $C^{46}H^{38}+2C^{46}H^{38}O^{3}+HO$ gives 82·88 carbon, 11·51 hydrogen, and 5·61 oxygen, which comes very near to the numbers obtained in the analysis of the Dammara resin.—*Pharm. Cent. Blatt.*, Dec. 22, 1847.

On the Digestion of Alcoholic Drinks, and their Function in Nutrition. By MM. Bouchardat *and* Saudras.

The authors have performed a series of experiments, with the view of ascertaining the mode in which alcohol is absorbed, and the changes which it undergoes in the system. Their first experiments were made upon dogs, which were killed two hours after the administration of a quantity of alcohol. The chyle and blood were separately examined for that fluid, which was found totally absent in the former, but present in minute quantity in the latter. Acetic acid was also detected in the blood by distillation with sulphuric acid, after the separation of the alcohol which it contained.

Owing to the difficulty in getting dogs to take spirituous fluids, they afterwards made use of fowls and ducks; and it was found that, in most cases where the blood was taken sufficiently soon after the administration of the alcohol, both that substance and acetic acid could be detected in it in minute quantity. Very rapid absorption also takes place, and in one experiment the authors found that three-fourths of the spirit administered was absorbed in less than twenty minutes.

It was then ascertained that the quantity of alcohol which escapes by the lungs is quite inconsiderable. This was determined by directing the gases and vapours evolved during respiration by a man who had taken a considerable dose of alcohol through a Woulff's bottle, surrounded by a freezing mixture. After the operation had been conducted for two hours, only a minute quantity of alcohol was found in the condensed fluid. None escaped by the urine or other secretions.

In the case of a man who, after a three days' debauch upon strong punch, was seized with a succession of epileptic fits, they found that blood drawn immediately from the jugular vein contained both alcohol and acetic acid in small quantity, while that taken an hour later contained none. They found, however, by Trommer's test, distinct

indications of the sugar which had been present in the punch, from which the authors draw the conclusion, that alcohol is digested more rapidly than sugar.

From these experiments the authors conclude that alcohol is absorbed by the veins, and not by the lacteals; and that, with the exception of the small quantity which escapes by the lungs, it is entirely oxidized into carbonic acid and water, either directly or by passing through the intermediate stage of acetic acid.—*Ann. de Chim. et de Phys.*, Dec. 1847, quoted in *Ed. Monthly Journal.*

Observations upon Crystallized and Amorphous Quinine and Cinchonine. By M. WINCKLER.

The results which the author has arrived at are of great interest, especially to pharmacologists, as they enable us to form a more accurate opinion of the value of quinoidine as a therapeutical agent. Winckler had occasion to observe that the crystallized cinchonine was converted into amorphous by the action of an excess of sulphuric acid, and at the same time found in the hyposulphite of soda a means of separating crystalline from amorphous quinine and cinchonine. According to his experiments, quinoidine contains amorphous quinine and cinchonine in variable proportions, according to the duration of the action of the acid in the preparation of these alkaloids and the nature of the barks. These results confirm, on the one hand, what Liebig first stated respecting the nature of quinoidine; and on the other, besides the discovery of amorphous cinchonine, point to those conditions by which, in the preparation of these alkaloids, the amorphous state may be avoided.

Some amorphous cinchonine was accidentally formed in the preparation of the sulphate of cinchonine, by adding a rather large quantity of concentrated sulphuric acid at once to the hot mixture, and then heating it somewhat strongly. In consequence of this treatment only one-third of the cinchonine separated subsequently in coloured crystals. On the subsequent addition of alkalies, a dark brown extremely-bitter substance resembling turpentine subsided, the solution of which in sulphuric acid was sent to the author for examination. The solution was diluted with water, filtered, and mixed with an excess of carbonate of soda. The separated mass was again dissolved in dilute sulphuric acid, treated as before with carbonate of soda, and now some sulphate of soda added to it, while the liquid was heated in the water-bath. On cooling, a considerable quantity of a nearly black mass had separated, while the supernatant liquid was pale brown. On the addition of ammonia this liquid now deposited an almost perfectly white pulverulent precipitate, which gradually aggregated to a dark yellowish-brown turpentine-like mass, which after sufficient washing with water was dried in the water-bath. In this state it exactly resembled the syrupy coloured residue, insoluble in pure æther, which remains when the extract of quinoidine with ordinary æther is treated after evaporation of the

latter with æther containing no water or spirit. Both were dissolved in absolute alcohol, and digested with animal charcoal at 104°, upon which both solutions were evaporated in the water-bath until their weight no longer varied. In this state both substances formed dark brown tenacious masses, which in thin layers were transparent, and which possessed an odour similar to commercial quinoidine. They dissolved in every proportion in strong alcohol, but not in æther and water. Equal quantities of the two substances saturated the same amounts of dilute acids, and were so completely precipitated from the solutions by carbonate of soda, that the liquid, after removal of the precipitate, was nearly void of taste and colour. Both substances behave precisely similar on being heated; they first melted, then disengaged some vapours of a bitter taste, and left a cinder which burnt without any residue, but with considerable difficulty. On cautiously heating some in a glass tube, a sublimate of crystals was obtained, which were exactly like those formed under similar circumstances from cinchonine. The peculiar odour of quinoile, which is perceived on heating crystallized and amorphous quinine, could not be observed. From solutions of the same amount of the two substances in muriatic acid, the author obtained the same weight of the insoluble platinum double salt, when an excess of chloride of platinum was poured into the solutions, which precipitated the whole of the organic substance from the liquids; however, the salts differed somewhat in their state of aggregation; that from quinoidine was of a bright yellow and loose, that from cinchonine was darker and more pulverulent crystalline. The double salt from cinchonine left on ignition 24·15 per cent., that prepared from quinoidine 23·35 per cent. of platinum. The author is thence led to believe that quinoidine (amorphous quinine and cinchonine) is formed by the action of acids upon the alkaloids in their preparation. He believes that quinine is not so readily converted by acids into amorphous quinine, as cinchonine, and a quinoidine containing but little or no amorphous quinine, is probably obtained in preparing a sulphate of quinine from barks containing both alkaloids.

Hyposulphite of soda immediately precipitates hyposulphite of quinine, in the form of a dazzling white crystalline precipitate, from the solution of the muriate of quinine; cinchonine separates under similar circumstances in four-sided needles. Both salts disengage sulphuretted hydrogen and sulphurous acid, when concentrated sulphuric acid is poured over them. When treated with dilute sulphuric acid, they are converted into sulphates, with evolution of sulphurous acid and elimination of sulphur. The amorphous alkaloids, when saturated with muriatic acid, do not yield these precipitates. The author turns this reaction to account in detecting the presence of crystalline alkaloids in quinoidine, and draws attention to the hyposulphites of the other vegetable bases.—*Jahr. für Prakt. Pharm.*, xv. p. 281.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Chromic Acid as a Bleaching Agent, and on a cheap and easy Means of recovering it. By CHARLES WATT, Sen.

CHROMIC acid has of late years become a very important agent in the bleaching of various articles, and particularly tallow and oils, more especially palm-oil. The best method therefore of using and then recovering it, so that it may again be employed, and the expense of the bichromate of potash, every time the chromic acid is required, be saved, cannot fail to prove of great advantage to all large consumers of this article.

About twelve years since, after numerous experiments and much application, I found that no agent was so effectual for bleaching foul, dark and offensive tallows and deep-coloured oils (namely, palm, linseed and rape oils) as the chromic acid. My only consideration therefore was, in what manner to obtain it in the cheapest form sufficiently pure for the intended purposes; and the deep red salt, the bichromate of potash, was that from the decomposition of which I obtained the acid, in the following manner:—

To bleach half a ton of dark tallow or high-coloured oils, from 5 to 10 lbs. of the bichromate of potash is required, and from it the chromic acid is liberated by decomposing the salt thus:—

The bichromate, well-bruised, is put into an earthenware, wooden or leaden vessel (not iron, as the acids act on it), and about 4 times as much hot water is then poured into it; the salt is then to be well-stirred; afterwards about $1\frac{1}{2}$ lb. of sulphuric acid (for every pound of bichromate) is carefully introduced, and the stirring is continued until the whole of the salt is dissolved. This liquid is chromic acid, mixed with sulphate of potash and an excess of free sulphuric acid, which is found greatly to assist in the bleaching.

The next part of the operation consists in introducing it into the tallow or oil, which, previously melted and well-settled from all extraneous vegetable and animal matters, and at about 130° F., is to be put into a vessel of wood capable of holding half a ton, leaving sufficient room for stirring. So soon as the liquid mixture of chromic acid, as before described, is poured into the tallow or oil, it is to be kept well-stirred until the whole of the colour is removed and a light pea-green has taken its place. The bleaching operation is now complete, and about four pailsfull of boiling water are to be poured in, and the stirring to be repeated for five minutes; the whole is then left to settle for about two hours, when it will be found quite white and fit for use.

It was formerly our custom to add about 4 or 5 lbs. of muriatic acid to the compound; but Mr. C. Watt, Jun., at the large factory of Messrs. Hawes, found that it increased the trouble and expense,

with no real benefit, and therefore he omitted it, and used only sulphuric acid to decompose the bichromate of potash.

The expense of bleaching one ton of bad tallow, or any deep-coloured oil, is about 1*l.*; it therefore became necessary to devise means of saving the chromic acid; and some years since I converted the oxide contained in the green liquid, left after bleaching, into chromate of lead; but it was found that this article would become so extensive in quantity, that all who used much chromic acid would be driven into another branch of business quite foreign to their usual occupation; and Mr. C. Watt, Jun., therefore devised the recovery of it into chromate of lime, equally as effectual as applied to bleaching, and much less expensive. His process is as follows:—

The green liquid, left after all the bleached oil is taken off, is put into another tub, and more water is added; then lime, made into a thick cream-like consistence, is gradually poured in till nearly all the sulphuric acid is saturated; the liquid is then run off into another vessel from the sulphate of lime, and into this liquid is to be gradually and carefully introduced some more of the cream of lime, till all the green oxide (powder) is precipitated and the liquor is clear and colourless; this liquor is to be drained off, and fresh water poured in, and, when settled, it is again to be poured off, and a fresh quantity put in, in order to wash the precipitate; this is at last to be dried, and then put on an iron slab, heated to redness, and kept frequently stirred. From a green it will be gradually changed into a yellow powder, which is the chromate of lime, and which, by being decomposed by sulphuric acid in such quantity as to leave an excess of free sulphuric acid, yields chromic acid, quite as well adapted for bleaching as that obtained from the bichromate of potash*. By this process the chromic acid can be recovered again and again, *ad infinitum*; and thus the method of bleaching by this agent is at once the most perfect and œconomical of any yet brought into operation†. It is almost needless to remark, that where, as in the great manufactories in Lancashire, much chromic acid is employed, this easy and cheap mode of recovering it will prove highly beneficial.

It may here be remarked, that several other methods of bleaching tallows and oils have since been tried. One consists in employing what is termed permanganic acid; but this agent so readily parts with its oxygen, that it is unmanageable, and is quite as expensive and much more troublesome. Another method is by blowing air through the goods, heated to a certain point. This also is found not so effectual as the chromic process, for there is considerable waste, and when made into soap the colour is much inferior.—Newton's *Journal*, March 1848.

* This process is perfectly identical with that described by M. Jacquelain in our fifth volume, p. 452.—Ed. *Chem. Gaz.*

† The patent for bleaching and purifying dark tallows and deep-coloured oils was taken out about twelve years ago by the writer.

PROCEEDINGS OF SOCIETIES.

Royal Society.

February 10, 1848.

(The Marquis of Northampton in the Chair.)

"Examination of the Proximate Principles of the Lichens." By John Stenhouse, Esq., Ph.D.

The author, after adverting to the labours of Robiquet, Heeren, Dumas, and Kane in the investigation of the proximate principles of the lichens, especially of those which yield red colouring matter with ammonia, and also of the more recent inquirers on this subject, such as Schunck, Rochleder, Heldt and Knop, who have greatly extended our knowledge of this interesting but difficult department of organic research, proceeds to state that nearly two years ago his attention was directed by Dr. Pereira to a kind of Orcella weed, which had been recently imported into London from the Cape of Good Hope, but which had been rejected by the London archil manufacturers as being unfit for their use, from the small quantity of colouring matter it yields when subjected to the usual process. With a view to ascertain whether or not the red dyes obtained from the various lichens result from the action of ammonia on a certain crystalline principle, described by Schunck under the name of *lecanorine*, the author procured quantities of the several lichens usually employed by the archil makers, and subjected them to investigation; the minute details of which, together with the results, are given at length in the present paper.

The specimens examined are the following:—

I. *South American variety of* Roccella tinctoria.

The lichen was cut into small pieces and macerated with a large quantity of water for some hours, then quick-lime was added. A yellow solution was obtained, from which muriatic acid precipitated the colouring matter, as a bulky gelatinous mass; this was washed, dried on a plate of gypsum, and dissolved in hot spirits of wine (not boiling). The solution on cooling deposited the colouring principle in small white prismatic needles arranged in stars. This is—

1. *Alpha-Orsellic acid* (hydrated) ..... $C_{32}H_{15}O_{13}+HO$

and its salt of baryta—

Alpha-Orselliate of baryta ..... $C_{32}H_{15}O_{13}+BaO$

2. *Alpha-Orselesic acid* was obtained by mixing crude gelatinous orsellic acid with a little water, neutralizing with lime or baryta, and precipitating with muriatic acid. A gelatinous hydrate is obtained, which may be purified by solution in dilute alcohol and crystallization.

The composition of this acid and its baryta salt is as follows:—

Alpha-Orsellesic acid ..... $C_{16}H_8O_7+HO$
Alpha-Orsellesiate of baryta $C_{16}H_8O_7+BaO$.

This acid gives a fugitive bluish-red or violent tint with hypochlo-

rite of lime. Orsellic acid gives a deep blood-red tint, quickly changing to yellow.

3. *Orsellesic ether*, $C_{16} H_8 O_7 + C_4 H_5 O$, is obtained from alpha-orsellic acid by boiling in strong alcohol, evaporating to dryness, and dissolving in boiling water. It crystallizes on cooling in long flat needles, having a yellowish colour from adhering resin.

II. Roccella tinctoria *from the Cape of Good Hope.*

By processes similar to those just mentioned, this lichen yielded—

1. *Beta-Orsellic acid*..... $C_{34} H_{17} O_{14} + HO$
   Beta-Orselliate of baryta .... $C_{34} H_{17} O_{14} + BaO$.
2. *Beta-Orsellesic acid* (formula to be given hereafter).
3. An ether compound, which is probably orsellesic ether. By three experiments its composition was found to be—

	I.	II.	III.
C	60·82	60·75	60·83
H	6·27	6·15	6·27
O	32·91	33·10	33·00
	100·00	100·00	100·00

4. *Roccellinine.*—Obtained by drying the gelatinous mass which is precipitated from the lime solution by muriatic acid, and boiling in strong spirit. The ether compound dissolves, and roccellinine remains behind. It is purified by repeated crystallization from strong spirit, aided by animal charcoal, and presents itself in soft hair-like crystals about an inch long, arranged in stars. It is a very indifferent substance, appearing however to be a feeble acid.

Its empirical formula is $C_{33} H_{17} O_{15}$.

III. *Roccella Montagnei.*

By similar treatment yielded—

1. *Erythric acid*..... $C_{20} H_{10} O_9 + HO$.

This acid gives a blood-red colour with hypochlorite of lime.

2. *Erythric ether* ..... $C_{20} H_{10} O_9 + C_4 H_5 O$.
3. *Erythric methylic ether* $C_{20} H_{10} O_9 + C_2 H_3 O$.

This ether crystallizes in longer and narrower prisms than erythric ether.

4. *Erythrelesic acid* is analogous to alpha- and beta-orsellesic acids.

5. *Picro-erythrine.*—By neutralizing erythric acid with lime or baryta, and throwing down erythrelesic acid with muriatic acid, a mother-liquid is obtained containing picro-erythrine, from which that substance may be separated in the form of yellowish crystals; and these may be purified and decolorized by repeated crystallization from hot water aided by the use of animal charcoal. Picro-erythrine gives a blood-red colour with hypochlorite of lime.

Its empirical formula is $C_{24} H_{24} O_{20}$.

6. *Pseudo-orcine*, of which the empirical formula is $C_{10} H_{13} O_{10}$. It is obtained by boiling the lime solution of *R. Montagnei* till it is re-

duced to one-fourth of its bulk, passing carbonic acid in excess through the liquid, and evaporating the filtered liquid to the consistence of a syrup; this is introduced into a flask and digested with a large quantity of ether, which dissolves orcine and leaves pseudo-orcine. On being crystallized two or three times from strong spirit, it is obtained in large shining colourless crystals. Still larger crystals may be obtained from an aqueous solution. Hypochlorite of lime has no action upon it.

The author then gives a mode of extracting the colouring principles of the lichens, so as to make them portable for commercial purposes. The extraction might be performed in the country where the lichens grow, by cutting them up into small pieces, macerating in milk of lime, neutralizing with muriatic or acetic acid, collecting the gelatinous precipitate on cloths, and drying it at a gentle heat.

He also suggests two modes of estimating the quantity of colouring matter in the lichens.

1. By macerating a known quantity of the lichen in milk of lime, and adding bleaching powder of known strength from an alkalimeter till all colour disappears from the liquid, and noting the quantity of solution required. It is thus found that—

Angola lichen requires.....	200	measures	1·00
American lichen requires.....	120	..	0·60
Cape lichen requires.....	35	..	0·17
Lecanora Tartarea (from Germany, near Giessen) requires.....	25	..	0·12

2. By extracting the lichen with milk of lime, precipitating with acetic acid, collecting the precipitate on a weighed filter, drying and weighing it.

IV. *Evernia Prunastri.*

1. *Evernic acid* is obtained by extracting the lichen with milk of lime, precipitating with muriatic acid, drying the precipitate, and digesting in weak spirit till nearly two-thirds are dissolved. The solution yields crystals of *evernic acid.* The insoluble part is usnic acid. Evernic acid yields only a slight yellow colour with hypochlorite of lime.

Formula of hydrated *evernic* acid ..	$C_{34}H_{15}O_{13}+HO$
Formula of everniate of potash	$C_{34}H_{15}O_{13}+KO$
Formula of everniate of baryta	$C_{34}H_{15}O_{13}+BaO+Aq.$

2. *Evernesic acid* is obtained by dissolving evernic acid in a slight excess of caustic potash, passing carbonic acid gas through the solution to saturation, and concentrating the solution: evernesiate of potash crystallizes out. From this the acid may be separated by means of muriatic acid. It gives a yellow colour with hypochlorite of lime.

Formula of hydrated acid.....	$C_{18}H_{9}O_{7}+HO$
Formula of evernesiate of baryta..	$C_{18}H_{9}O_{7}+BaO+Aq.$
Formula of evernesiate of silver ..	$C_{18}H_{9}O_{7}+AgO.$

Orcine.

This substance is always obtained when any of the colouring principles of the lichens which yield red dyes with ammonia are subjected to particular processes. The best way of obtaining it pure is to boil the alpha-, or beta-orsellesic acid, or the erythrelesic acid in water for about an hour. Carbonic acid is given off, and crystals of colourless orcine are deposited. It gives a dark purple red colour with hypochlorite of lime, quickly changing into deep yellow.

Empirical formula..... $C_{16} H_{11} O_7$.

Brom-orceide, $C_{16} H_{24} Br O_{13}$ (empirical), is obtained by pouring bromine into a concentrated aqueous solution of orcine; when pure it forms long white adhering needles; it has no taste or smell.

Chlor-orceide, a similar compound, is obtained by passing chlorine gas through a solution of orcine.

Usnic Acid.

This principle is found in *Usnea florida, U. hirta, U. plicata, U. barbata, Ramalinea calicaris, R. Fraxinia, Evernia Prunastri,* and *Cladonia Rangeferina.* It is best obtained from *Cladonia Rangeferina* and *Usnea florida,* by the use of lime and muriatic acid.

Its empirical formula is $C_{38} H_{17} O_{14}$.

PATENT.

Patent granted to Theodore Fletcher, Birmingham, *for an improved Manufacture of Speculums.*

This invention consists in coating the backs of glasses, which have been "quicked or silvered" for the purpose of forming speculums (such as mirrors, looking-glasses or reflectors), with metal by the electrotype process, whereby the quicksilver will be protected from injury, and a stronger power of reflecting light will be given to the speculum.

The patentee takes a glass plate, which has been silvered, and lightly and carefully coats the back or silvered side of the same with a varnish, composed of 2 oz. of shell-lac, $\frac{1}{2}$ pint of highly-rectified spirits of wine, and $\frac{1}{2}$ oz. of the best lamp-black; this varnish protects the quicksilver from damp, and from the action of the acid used in the subsequent process. Before the varnish has become hard, he shakes over it, from a fine muslin bag, some finely-pulverized black lead, or black oxide of manganese, or other metallic oxide or powder, or covers it with leaf metal, so that the whole surface which has been varnished will be covered with a perfect but thin coat of metal; he then submits the glass plate to the electrotype process; and by this means a thin coating of copper or other metal will be precipitated over the entire back of the plate.—Sealed Aug. 3, 1847.

THE CHEMICAL GAZETTE.

No. CXXXI.—April 1, 1848.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Asparagine and Aspartic Acid. By Prof. R. Piria.

In the following memoir the author shows,—1st, that asparagine, which was discovered in 1815 by Robiquet and Vauquelin in asparagus, and subsequently in several other plants, for instance in Althea, the potato, beet-root, and in vetches grown in the dark, is contained most abundantly in the vetch; 2nd, that the asparagine does not pre-exist in the seed of the vetch, but is evolved on germination both in the dark and when exposed to light, and again disappears when the plant flowers; 3rd, that asparagine is an acid, and not, as hitherto admitted, a neutral substance; it expels the acid from acetate of copper; 4th, that asparagine dissolved in water experiences, in the presence of the juice of the vetch, a kind of fermentation when, assimilating 4 equivs. hydrogen and 2 equivs. oxygen, it passes into succinate of ammonia; 5th, that on boiling with nitric acid free from hyponitric acid, or with muriatic acid, it is converted into ammonia and aspartic acid; while on fusion with hydrate of potash, it is transformed, with disengagement of hydrogen, into ammonia, acetic and oxalic acids; 6th, that asparagine and aspartic acid, on treatment with hyponitric acid, are metamorphosed, after the manner of the amides, into water, nitrogen and malic acid; so that they may be regarded as two amides of malic acid, which correspond to the amides of oxalic acid, viz. oxamide and oxamic acid.

The preparation of asparagine is very simple; the juice of the plant is heated to boiling, freed from the albumen which separates, and evaporated. The crystals formed in the syrupy residue are collected and purified by recrystallization. Not a trace of asparagine was obtained by this process from the seed; while young plants which had been grown from seed in a dark chamber, as well as young vetches which had grown in the open field, afforded a very large quantity of the most beautiful crystals, which completely resembled sugar-candy. More developed plants, such as already showed flower-buds, merely yielded a trace of asparagine, and in those in fruit no longer a trace was to be found. The analysis of the asparagine prepared from vetches furnished 31·80 carbon, 6·85 hydrogen, 18·84 nitrogen, and 42·51 oxygen, which agrees with the known composition of this substance.

Asparagine and Oxide of Copper, $C^8 H^7 N^2 O^5$, CuO.—Asparagine reddens litmus-paper and expels acetic acid from the acetate of copper. When oxide of copper is heated with a solution of asparagine in water, or a hot concentrated solution poured into an equally hot and concentrated solution of acetate of copper, a light blue precipitate falls of a combination of asparagine with oxide of copper, which is insoluble in cold, slightly soluble in hot water, and readily soluble in acid and ammonia. At 248° this compound loses no water; at a higher temperature it disengages a current of ammonia. From the following analysis it will be seen that asparagine, dried at 212°, and hitherto considered anhydrous $C^8 H^8 N^2$, still contains 1 atom of water, which can be replaced by a metallic oxide:—

Carbon	29·30	29·42	29·35	8	29·50
Hydrogen	4·41	4·51	4·36	7	4·30
Nitrogen.....	17·25	17·25	17·25	2	17·21
Oxygen	24·64	24·43	24·65	5	24·58
Oxide of copper..	24·40	24·38	24·39	1	24·41

To determine with certainty whether the asparagine was really contained as such in this compound, a quantity of it was diffused in water, and decomposed with sulphuretted hydrogen. From the filtered liquid, which had an acid reaction, crystals of asparagine separated in an unaltered form, the analysis of which again gave 32·09 carbon, 6·79 hydrogen, 18·80 nitrogen, and 42·32 oxygen. This is the composition of asparagine dried at 212°, whose formula therefore, if the copper compound = $C^8 H^7 N^2 O^5$, CuO, becomes $C^8 H^7 N^2 O^5 + HO$.

Action of Ferments upon Asparagine.—While perfectly pure asparagine may be kept, without undergoing the least alteration, in solution, it is decomposed when the crystals are still coloured by the juice of the vetch, or still more readily if some of the vetch juice is added to the solution; the liquid soon loses its acid reaction and becomes faintly alkaline, diffuses an odour of putrefying animal substances, and becomes covered on the surface with a white mucilaginous pellicle, in which numbers of infusoria occur. In the course of a short time the asparagine has entirely disappeared, and in its place we find succinate of ammonia, or at least a substance which, on treatment with acids, is decomposed into these two constituents. Both are found in the residue left on evaporation of the liquid to which muriatic acid had been added. The acid afforded on analysis—

Carbon.....	40·27	40·40	4	40·68
Hydrogen	5·28	5·16	3	5·08
Oxygen	54·45	54·44	4	54·24

If we subtract from the elements $C^8 H^{12} N^2 O^8$ (succinate of ammonia) those of asparagine, $C^8 H^8 N^2 O^6$, there remain $H^4 O^2 = 2HO + H^2$; whence it follows that asparagine assimilates 2 equivs. of water and 2 equivs. of hydrogen in order to pass into succinate of ammonia. It was found impossible to convert the succinate of ammonia again into asparagine by oxidizing agents.

Action of Acids and Alkalies upon Asparagine.—It is well known that asparagine is converted, under the influence of acids and bases, into ammonia and aspartic acid, $C^8 H^7 NO^8$. Piria obtained, upon evaporating crystalline asparagine with muriatic acid, chloride of ammonium and aspartic acid, which underwent no change on again treating the residue with muriatic acid. It dissolves very readily in muriatic acid, crystallizing only when the liquid is evaporated to a syrup, while it is scarcely soluble in cold water. It very tenaciously retains the muriatic acid; and after drying at 212°, still contains muriatic acid and absorbs water. A new acid is stated to be formed by this treatment, but most probably this behaviour of the impure aspartic acid has led to this error. On treating asparagine with pure nitric acid of moderate concentration, nitrate of ammonia and aspartic acid are formed; but other products originate if the nitric acid contain hyponitric acid. The analysis of the aspartic acid obtained with nitric acid agrees, as will be seen from the following numbers, with those of other chemists:—

Carbon.....	35·99	8	36·09
Hydrogen.....	5·47	7	5·26
Nitrogen	10·78	1	10·73
Oxygen.....	47·76	8	48·12

If nitrate of lead be added by degrees to the liquid obtained on treating asparagine with nitric acid after neutralization with ammonia, a double salt is formed of aspartate and nitrate of lead, which is sparingly soluble, resembles the crystallized formiate of lead, and explodes gently when heated. It experiences no loss on being dried in a current of air at 302°, and has the formula

$$2PbO + C^8 H^5 N^2 O^{12} = PbO\,HO + C^8 H^5 NO^6\,PbO, NO^5.$$

The production of this double salt appears however to depend very much upon certain proportions of the components and the degree of concentration of the liquid; for notwithstanding repeated experiments, the author could not succeed in obtaining it a second time. The results of the analysis of this double salt are—

Carbon.....	11·96	12·00	8	11·97
Hydrogen	1·63	1·62	6	1·49
Nitrogen	7·36	7·21	2	6·98
Oxygen	23·57	23·72	12	23·94
Oxide of lead	55·48	55·45	2	55·62

It has been stated above, that nitric acid containing hyponitric acid furnishes different products. Nitrogen is disengaged, proceeding from the further decomposition of the ammonia produced by the decomposition of asparagine into aspartic acid and ammonia; but, on the other hand, also from the aspartic acid, as this, when treated alone with nitrous acid, also disengages nitrogen. It was therefore probable that asparagine and aspartic acid contained one and the same group of organic elements conjoined with different amounts of ammonia. To test this view, 17·5 grms. asparagine were dissolved in 70 grms. nitric acid of 25° Beaumé, upon which a current of deut-

oxide of nitrogen was passed into the solution. A reaction immediately resulted, which soon became very lively, while the temperature rose some degrees. The current of nitric oxide was continued until no more gas was disengaged. The liquid was now coloured dark green, from the nitrous acid it contained, and was saturated with pieces of marble. A solution of acetate of lead threw down a white precipitate from the still faintly acid liquid, which soon diminished in volume, becoming crystalline with a lustre of mother-of-pearl. On treating these crystals with hot water, a small portion dissolved, and again separated in crystals as the solution cooled. The greater portion remained undissolved, forming a yellow semi-fluid viscous mass. It was evident, from this behaviour, that this substance was malate of lead. After decomposing it with sulphuretted hydrogen, and evaporating the liquid, the residue had all the properties of malic acid. An analysis of the lead compound yielded moreover the following numbers, which correspond to the formula $2PbO + C^8 H^4 O^8 + 6HO$:—

Carbon.....	12·21	12·18	8	12·21
Hydrogen	2·47	2·52	10	2·54
Oxygen	28·66	28·64	14	28·51
Oxide of lead	56·66	56·66	2	56·74

It must be concluded from the preceding, that muriatic and nitric acids convert asparagine, with the assistance of heat, into aspartic acid, but no further; while both asparagine and aspartic acid are converted with the greatest ease into malic acid by nitrous acid, nitrogen being given off. If we add 2 equivs. water to the elements of aspartic acid ($C^8 H^7 NO^8$), we obtain the composition of the bimalate of ammonia,

$$C^8 H^7 NO^8 + 2HO = C^8 H^4 O^8, HO, NH^4 O.$$

On the other hand, we obtain the composition of the neutral malate of ammonia by adding 4 equivs. water to the elements of asparagine,

$$C^8 H^8 N^2 O^6 + 4HO = C^8 H^4 O^8, 2NH^4 O.$$

Asparagine and aspartic acid may therefore be regarded as two amides of malic acid; the evolution of nitrogen and the whole reaction of nitrous acid is readily explained from the behaviour of this acid towards ammonia in the nascent state. The same relation consequently exists between malic acid, aspartic acid and asparagine as between oxalic acid, oxamic acid and oxamide. We have—

$C^4 NH^5 O^8$ binoxal. ammon.	$2HO = C^4 NH^3 O^6$ oxamic acid.
$C^4 N^2 H^8 O^8$ neutr. oxal. ammon.	$4HO = C^4 N^2 H^4 O^4$ oxamide.
$C^8 NH^9 O^{10}$ bimal. ammon.	$2HO = C^8 NH^7 O^6$ aspartic acid.
$C^8 N^2 H^{12} O^{10}$ neut. mal. ammon.	$4HO = C^8 N^2 H^8 O^6$ asparagine.

The author compared the behaviour of nitrous acid towards oxamide, succinamide and butyramide. Nitrogen was given off in all cases, and oxalic acid, succinic acid and butyric acid formed. It appears therefore that this reaction is peculiar to all the amides; and it is extremely probable that important results will be obtained by the action of nitrous acid on other nitrogenous bodies. The ease

with which the metamorphosis takes place deserves especial attention. Acids and alkalies in many cases only convert the amides into ammoniacal salts at a high temperature; with nitrous acid they yield the acid from which they originated at the ordinary temperature. This is the case with aspartic acid; with nitrous acid it very readily affords malic acid, with evolution of nitrogen; while, on fusing it with potash, it is converted with great difficulty and imperfectly; the temperature at which it separates into ammonia and malic acid is situated so high, that the latter is itself decomposed into acetic and formic acids. When an excess of potash was used, malic acid could never be detected in the residue; while this contained acetate and oxalate of potash if the treatment was discontinued as soon as the evolution of ammonia ceased.—*Ann. de Chim. et de Phys.*, xxii. p. 160.

On the Action of Hydrosulphuric Acid upon Nitrocumene and Binitrocumene, and on the Formation of Alkaloids analogous to Aniline and Nitraniline. By A. Cahours.

In an investigation which I had the honour of communicating to the Academy relative to the action of fuming nitric acid upon organic substances*, I stated that cumene, $C^{18}H^{12}$, might, according as it was treated with nitric acid alone or with a mixture of this acid and Nordhausen sulphuric acid, give rise to compounds which could be represented by the formulæ $C^{18}H^{11}(NO^4)$ and $C^{18}H^{10}(NO^4)^2$, which we shall call, in accordance with the notation of M. Gerhardt, nitrocumene and binitrocumene. When the action of nitric acid upon cumene is continued for some length of time, nitrobenzoic acid is formed, as was discovered by M. Abel.

The analogy which exists between cumene and benzene led me to imagine that the preceding nitrogen compounds would behave towards hydrosulphate of ammonia in the same manner as nitrobenzene, and furnish alkaloids analogous to aniline and nitraniline. These views have been completely confirmed by experiment.

When a current of sulphuretted hydrogen is passed into an alcoholic solution of nitrocumene to which ammonia has been added, the substance is very slowly attacked, yielding a basic product, which saturates acids and forms crystalline compounds. I have not been able to procure this substance in sufficient quantity to purify it and submit it to analysis. It is probable that the substance formed under these circumstances is *cumine*, $C^{18}H^{13}N$, the homologue of aniline, $C^{12}H^7N$.

If, instead of nitrocumene, binitrocumene is employed, it is most readily acted upon by the hydrosulphate of ammonia, and is quickly and entirely converted into a crystalline alkaloid, furnishing beautifully crystalline salts with a large number of acids. In the pure state the new base forms yellowish scales, which melt at a tempera-

* Chem. Gaz., vol. v. p. 213.

ture below 212°, and solidify on cooling to a radiated mass of needles. It is insoluble in water, but dissolves readily in alcohol and æther; it undergoes a partial alteration on distillation, but the greater portion passes over unaltered. Its alkaline reaction towards coloured tests is slight, but perceptible; it completely neutralizes the strongest acids. On analysis it furnished—

Carbon	59·79	18	= 108	60·0
Hydrogen	6·63	12	12	6·7
Nitrogen.....	15·71	2	28	15·6
Oxygen	..	4	32	17·7

This compound may be considered to be derived from cumene, in which 1 equiv. of hydrogen is replaced by 1 equiv. of hyponitric vapour, for which reason we shall call it *nitrocumine*. This alkaloid combines readily with hydrochloric acid, forming a salt, which is deposited from a saturated solution, on slow cooling, in white silky needles. Dried by exposure to the air, this salt furnished results leading to the formula $C^{18} H^{12} N^2 O^4$, ClH + 2HO. The sulphate is obtained by dissolving the base in warm dilute sulphuric acid. On slow cooling, the salt separates in the form of long, very brilliant prisms, which may be very easily reduced to powder. According to analysis this salt is represented by the formula $C^{18} H^{12} NO^4$, SO^3 + 2HO. The nitrate crystallizes on cooling in silky needles of a dazzling white when pure, the oxalate in the form of slender needles. All these salts are rapidly altered when moist or in solution by exposure to the air, when they assume a greenish-blue colour; the double salt with chloride of platinum crystallizes in orange-coloured needles, which are very quickly decomposed.

Bromine acts violently on nitrocumine, and furnishes a crystalline compound, which no longer possesses basic properties.

In the presence of chloride of benzoyle, nitrocumine undergoes no change in the cold; but as soon as the temperature is raised to between 122° and 140°, a violent reaction ensues, and a product is obtained, which, after washing with acidulated, then with alkaline water, and lastly with pure water, dissolves readily in boiling alcohol, and separates almost entirely on cooling in dazzling white needles. On analysis this compound yielded numbers leading to the formula $C^{32} H^{16} N^2 O^6 = C^{14} H^5 O^2$, $C^{18} H^{11} N^2 O^4$.

If we represent nitrocumine, $C^{18} H^{12} N^2 O^4$, by Cn, we have $Cn - H = C^{18} H^{11} N^2 O^4$, which would correspond to $Am - H = NH^2$, or amidogen. The preceding compound would consequently be the analogue of benzamide and benzanilide.

The chlorides of cinnamyle and of cumyle furnish analogous compounds by contact with nitrocumine.

The preceding results demonstrate therefore that nitrocumene and binitrocumene, the homologues of nitrobenzene and binitrobenzene, furnish, like the latter, under the influence of hydrosulphuric acid, bases which may be regarded as the homologues of aniline and of nitraniline.—*Comptes Rendus*, March 6, 1848.

On Errors in the Determination of the Specific Gravity in finely-divided Bodies. By Prof. G. Rose.

On repeating some former experiments on the specific gravity of gold and silver, the author obtained such different results according as the determinations were made with fused, compressed or powdered metals, that he was induced to extend his inquiry to other substances. With this view he selected platinum and sulphate of baryta, in which the same result was obtained. The cause appears therefore to be a general one.

Specific Gravity of fused Gold.—These determinations are accompanied with great difficulties, as it is scarcely possible to obtain the gold in a suitable state. Native gold always contains silver, with slight traces of iron and copper; and in the larger masses of native gold, quartz and brown iron ore are frequently enclosed. The purified gold, fused in crucibles, is always full of smaller or larger cavities, whether melted alone or beneath layers of borax, carbonate of soda or chloride of sodium. When melted alone, a large hole is found on the under surface if it solidified quickly, because fused gold occupies a much larger space than the solidified. Such a cavity frequently extends far beneath the surface, and in such case it is impossible to expel all the air. Moreover, the metal appears covered on the surface by frequent rows of very minute crystals, which intersect at an angle of 60°, and leave minute cavities between one another. If the fused gold is allowed to cool slowly, for instance, when melted in a porcelain furnace, its surface is found to be still more distinctly crystalline. If fused under a stratum, the surface is, it is true, smooth and bright; but in this case deep cavities occur, which are filled with the flux. All these errors could only be avoided by determining the specific gravity of the metal, and of other metallic alloys, after they had been passed through the pressing machine of the mint.

At a temperature of 14° R. the author obtained the following numbers in his new experiments. Gold, fused in a clay crucible with borax and nitre, possessed a specific gravity of 19·2089; after it had been pressed, 19·3202; after being fused again in a black-lead crucible, 19·2908; and after repeated pressure, 19·3296. Since Marchand and Scheerer found that copper fused under a stratum of chloride of sodium possessed a higher specific gravity than when fused under other strata, a regulus was fused under a layer of chloride of sodium. Its specific gravity was 19·2722; after pressure, 19·2992; after fusion in a black-lead crucible, 19·2955; and after being pressed again, 19·3087. Gold, reduced by means of oxalic acid and fused in a black-lead crucible, had a specific gravity of 19·2981; and after pressure, 19·3336. The fusion of gold under a layer of chloride of sodium did not afford the means therefore of obtaining gold of greater density; as it likewise remained lower after pressure, it appears as if the gold enclosed particles of chloride of sodium. Apparently that gold has the highest specific gravity which has been melted of itself in a black-lead crucible, and submitted to

pressure. The author consequently assumes preliminarily 19·3336 as the specific gravity of gold at 14° R.

Specific Gravity of Silver.—Native silver cannot be employed to determine the specific gravity, because it is never pure; and that which has been purified cannot be melted alone for this purpose, because on cooling, a portion is projected, and it puffs up more or less. The determinations made by Bresson are for this reason too low. In his former experiments, the author weighed the regulus obtained on reducing the chloride, which answers very well. The earlier results with three different samples were,—I. 10·5041, II. 10·4991, III. 10·5036. In his recent experiments, the regulus II. was fused in a clay crucible beneath a stratum of common salt. The regulus obtained was smooth on the upper surface, but reticulate on the lower one, and was consequently filed away at this place. Its specific gravity agreed with the results of the former experiments, being 10·5050 at 14° R.

Specific Gravity of Gold in the State of Powder.—Gold precipitated by protosulphate of iron from dilute solutions appears amorphous under a high magnifying power, on account of its minute state of division. From concentrated solutions it is precipitated in microscopic cubes. Gold reduced by oxalic acid appears in more distinct crystals; they are octahedrons. The metallic film deposited on the sides of the vessel in which the reduction is made, consists entirely of such crystals. The results given below exhibit great differences, which can however only be ascribed to the nature of the precipitate, as several samples of the same precipitate afforded results which agreed with each other. The highest specific gravity was found in the finely-divided precipitates; for the larger the precipitated particles are, the lower the specific gravity. The specific gravity of gold, as precipitated by sulphate of iron, was found to be at 14° R. 19·5701, 19·7447, 19·8150, 20·6882, 20·2634. That precipitated with oxalic acid weighed likewise at 14° R. 19·4791; gold filings afforded at 16°·9 R. yielded the low specific gravity of 19·2178 Little globules, of about the size of a pin's head, fused before the blowpipe, likewise gave only 19·2721 at 18°·2 R. It is of no great consequence whether the surface of the metallic particles had been dried before immersing them in the water, as they are completely moistened when boiled with water. The precipitate which had given the above specific gravity of 19·5701 yielded, after drying and subsequent boiling with water, 19·5622; the dried precipitate, when pressed, possessed the specific gravity of 18·0194 only.

Specific Gravity of Silver in the State of Powder.—The silver employed by the author was precipitated from a solution of the nitrate by protosulphate of iron. The precipitate consisted of microscopic crystals, which were in general larger than in the case of the gold; they are octahedrons with truncated edges; they afforded at 14° the numbers 10·5485 and 10·6139. In this case also the lowest specific gravity was possessed by the coarsest precipitate.

Specific Gravity of Platinum in a State of Powder.—This is stated by Playfair and Joule to be 17·890. Liebig gives that of

platinum-black at 17·572, 17·580, 16·1319. Platinum-black, prepared by Mitscherlich by precipitating chloride of platinum with carbonate of soda and sugar, and which appeared amorphous under the highest magnifying power, had the high specific gravity of 26·1418 at 14°; while that of platinum foil, according to various determinations, is situated between 21° and 22°.

Specific Gravity of Native Sulphate of Baryta.—The specific gravity of a crystal from Silbach in Westphalia was 4·4875; another crystal, from the same locality, 4·4855; a crystal from Przibram, 4·4808; a crystal from Champeix in Auvergne, 4·4798; several fragments from the same locality, 4·4808; the largest of the latter, 4·4776 at 14° R. The heavy spar of Silbach afforded, according to an analysis made by Rammelsberg, 99·40 per cent. pure sulphate of baryta and 0·60 sulphate of strontia and baryta, and may therefore be considered as pure sulphate of baryta. The specific gravity of the sulphate of baryta, precipitated from the chloride by sulphuric acid, and which consisted of microscopic prisms, amounted at 14° R. to 4·5209 and 4·5350. Finely-pulverized native heavy spar from Champeix possessed a specific gravity of 4·48447; some from Dufton, 4·8027; both powders appeared very coarse under the microscope, in comparison with the precipitated salt.

Conclusions.—1. Determinations of the specific gravity of substances, obtained in a finely-divided state by precipitation, generally come out higher than when large crystals or solid masses are weighed. 2. In the first of these cases, the specific gravity increases with the greater state of division of the precipitate. The reason of this is, that the increased surface of the body condenses more water upon it than upon a smaller one, precisely in the same manner as solid bodies act towards gases; consequently it is not only the body which is weighed in water, but at the same time also a surrounding stratum of denser water; and in this manner too low a number is obtained for the loss in water, which, on division into the absolute weight of the body, affords too high a result. Even though the water is but slightly compressible, yet to this circumstance must be opposed the very considerable power of condensation of finely-divided bodies, which is certainly great in specifically heavy bodies, bearing in mind that box-charcoal absorbs thirty-five times its volume of carbonic acid. Since the precipitated metals possess the same crystalline form as when fused, at least in the case of gold and silver, the higher specific gravity cannot be owing to the matter of the precipitated metal, and must consequently rather be sought for in the above causes. In the case of the sulphate of baryta the result is not quite so decisive, although even here the precipitated salt has a higher specific gravity, because it could not be determined whether the crystals of the precipitated salt were of the same form as the native. But that the gold filings and the pulverized heavy spar had not a higher specific gravity, is probably owing to its being impossible to accomplish by mechanical means the requisite degree of division. To obviate the mischievous influence of cavities which occur in native minerals, it has become since Beudant, generally the

custom to use the powdered mineral for determining the specific gravity. According to the above experiments, there is no objection to this, as the state of pulverized substances can have but little influence on the specific gravity. The determinations in the case of chemical precipitates, which give erroneous results, are, from its being frequently impossible to obtain pure substances in any other manner than by precipitation from a solution, so important, that the discovery of an accurate method for the determination of their specific gravities would be of great value.—Poggendorff's *Annalen*, lxiii. p. 1.

On the Bile of the Pig.
By Dr. C. Gundelach *and* Dr. A. Strecker.

Thenard's investigation made us acquainted with the fact, that the bile of the pig is precipitated by acetic acid. Gorup-Besanez has recently asserted that the acid of this bile is choloidic acid, as it possesses the same reaction and composition. The authors have submitted this bile to a more minute examination; they give a description of the properties of the bile itself, with its analysis, and further show that the principal constituent is a peculiar new acid, hyocholic acid, which resembles choloidic acid, but is decidedly distinct. No taurine occurs in pig's bile; it cannot be formed from hyocholic acid, because this contains no sulphur, in which respect, as well as by its insolubility in water, it essentially differs from bilic acid. Weak acids, even the gastric juice of a dog, decompose pig's bile, and separate the hyocholic acid; so that the acid properties of the food must be destroyed in the alimentary canal.

Properties of Pig's Bile.—This bile forms a brownish or yellow liquid, which has at first a sweetish, but afterwards a strong bitter taste. Its reaction is very faintly acid. When distilled at 221° F. in a chloride of calcium bath, a slightly turbid liquid of a most disagreeable odour passes over, which is alkaline from the presence of ammonia, and contains a small quantity of a volatile fatty substance, which can be collected by agitation with æther, and is left, on evaporation of the æther, with a disagreeable odour of pigs. It is very difficult to dry pig's bile in the water-bath so as to reduce it to powder; it lost on an average, after long-continued drying, 88·8 per cent. of water, which is less than that of ox-bile, which contains 92·93 per cent. The dry powdered bile dissolved, with the exception of 0·56 per cent. of coagulated mucus, in absolute alcohol.

Proximate Constituents of Pig's Bile.—After standing for a considerable length of time at a temperature below 32°, the chloride of sodium separated from the alcoholic solution of the dry bile; it was removed, the solution decolorized by digestion with animal charcoal, filtered, and precipitated with æther as long as any turbidness resulted. The æther separates the hyocholate of soda (which contains some potash and ammonia) in the form of a resin, which is several times treated with æther. The æther used for this purpose is added to the alcoholic liquid decanted from the hyocholate of soda. After distilling off the æther and alcohol, crystals of choles-

terine separate from the aqueous residue; they are obtained perfectly pure by recrystallization from alcohol, which retains in solution the fat of the bile and some hyocholate of soda. The hyocholate of soda, as thus obtained, has a yellowish colour, from which, and likewise from chloride of sodium, it can be freed by re-solution in absolute alcohol, digesting the solution with animal charcoal, and precipitation with æther. It forms the chief constituent of pig's bile; for on treating fresh bile with absolute alcohol and æther, 7·9 per cent. of dried precipitate were obtained, which, calculated for dry bile, amounts to 74·8 per cent. The quantities of the proximate constituents of the dry bile are consequently 5·3 per cent. substance insoluble in alcohol, principally mucus of the gall-bladder, 74·8 per cent. crude hyocholate of soda, and 19·9 per cent. fat and cholesterine still containing some hyocholic acid. It is consequently evident from this constitution, that the principal properties of the pig's bile must depend on the substance precipitated by æther from the solution in absolute alcohol.

Properties of the crude Hyocholate of Soda (free from fat and mucilage).—In the state in which it is precipitated from the alcoholic solution, it still contains small quantities of other substances. When dried between 230° and 248°, it leaves 11·4 per cent. of ash, consisting principally of carbonate of soda, together with chloride of sodium, phosphate of lime, magnesia, manganese and some potash; it likewise contains some sulphuric acid. Its alcoholic solution has an acid reaction; on adding acids to this, nearly the whole of the organic substance is precipitated, and the solution contains scarcely anything more than the soda, potash and ammonia salt of the acid added. On drying at 230°, the mass, which still contains some alcohol, first melts without being decomposed, and puffs up considerably, owing to the escape of the alcoholic vapour, when it gradually becomes hard, and may now be easily pulverized. The powder no longer cakes together at 230°. It is tolerably white, with a faint tint of yellow, does not become moist in the atmosphere, and dissolves wholly in water and alcohol. The solutions have a strong bitter taste. Dilute acids, even organic, separate the hyocholic acid in the form of an adhesive resin. The aqueous solution of the bile, freed from fat and mucilage, affords with chloride of calcium, sulphate of magnesia and chloride of barium white flocculent precipitates, which dissolve in boiling water, and again separate partially on cooling. Perchloride of iron yields yellowish-white flakes, which become reddish-brown on boiling. Oxide of copper yields a bluish-white, corrosive sublimate a white, protoxide of mercury a gelatinous precipitate, which subsides in flakes on boiling. With neutral acetate of lead a flocculent precipitate is obtained, which does not cake together on boiling (after the precipitation the liquid has an acid reaction, and upon the addition of ammonia affords a further precipitate; a portion of the lead salt remains dissolved); with chloride of zinc and sulphate of the protoxide of manganese, white flocculent precipitates; with nitrate of silver a white gelatinous precipitate, which may be boiled in the liquid without in the least

turning brown as long as no excess of nitrate of silver is present. A moderately-concentrated alcoholic solution of the principal constituent of the bile affords no precipitate with any of the preceding reagents.

If a concentrated solution of an alkaline salt, whether of potash, soda or ammonia, with any acid, carbonic acid or sulphuric acid, &c., or even caustic potash or soda, is added by degrees to a tolerably-concentrated solution of pig's bile, or to the bile itself, a turbidness at first results on the addition of each drop, which again disappears on agitating the solution. If the addition is continued, re-solution no longer takes place, and a colourless flocculent precipitate is obtained. The colouring substance present in the bile remains in solution; and the precipitate appears, after washing with the solution employed for precipitation, perfectly colourless. If, on the contrary, the solution of the bile is added by degrees to the solution of an alkaline salt, the first drops produce a permanent precipitate. The precipitates which are caused by salts, potash or soda, exhibit no trace of crystallization under the microscope, while the precipitate produced by ammoniacal salts consists of microscopic needles. The precipitate always contains the alkali used for precipitating, and on boiling the liquid it mostly dissolves, and again falls on cooling in flakes. This behaviour is very easily explained; the hyocholates resemble many soaps, which are readily soluble in water, but dissolve with great difficulty in solutions of salts of the alkalies or their hydrates; consequently, upon the addition of an alkaline salt to a concentrated solution, a precipitate results, which disappears on agitation, until the solution contains a sufficient quantity of the alkaline salt, whereupon the salt of that base separates which is present to the largest amount, *i. e.* the salt of the alkali employed for the precipitation. The ammonia salt, prepared in this manner by precipitating the bile with chloride of ammonium, contains mere traces of ash.

Composition of the crude Hyocholate of Soda.—Of the inorganic constituents above-mentioned, the chloride of sodium was determined by decomposing the bile with nitric acid, and precipitating the chlorine as chloride of silver, as on reducing the bile to ash chloride of sodium is likely to be volatilized. In this manner the author found 0·45 per cent., 0·48, and a third time 1·5 per cent. chloride of sodium. The sulphur amounted only to 0·47 per cent., and was due to sulphates existing in the bile. The analyses of the substance dried between 230° and 248° yielded the quantities enumerated under I. II. and III., which, after deducting the above-mentioned quantities of chloride of sodium, viz. 1·5 from the ash of No. I. and 0·5 from that of II., lead approximatively (as some potash is likewise contained in the ash) to the composition given under A.:—

	I.	II.	III.	A.
Carbon	64·17	64·45	64·65	65·1
Hydrogen	8·76	8·75	8·76	8·9
Nitrogen.....	3·21	3·42	..	3·3
Oxygen	..	..	..	16·6
Ash.....	11·66	11·40	NaO	6·1

Pure Hyocholate of Soda, $C^{54}H^{43}NO^{10} + NaO$.—On digesting fresh bile with sulphate of soda and a little water, in proportion as the liquid becomes saturated with the salt, impure hyocholate of soda, still containing mucus and colouring matter, separates. The precipitate is collected on a filter, and washed with a saturated solution of sulphate of soda, when it is dried at 212°, and the hyocholate of soda extracted with absolute alcohol. The solution is but slightly coloured; it is treated with animal charcoal, and then mixed with æther, when the salt separates perfectly white. About 5·2 per cent. of pure salt is obtained in this manner from the fresh bile; there consequently remains 2·7 per cent. in the solution of sulphate of soda, which consists however principally of colouring substance, fat, chloride of sodium and mucus. These substances separate on evaporation in the form of a brown pellicle; so that when the liquid is evaporated about one-half, it contains scarcely any organic matter. After desiccation at 212°, the precipitate may readily be reduced to a snow-white powder, which easily redissolves in alcohol, and on evaporation leaves a colourless varnish. It has a lasting bitter taste, unaccompanied by the slightest sweetness; its solutions are neutral, and furnish the same reactions as those described under the impure salt. Heated upon platinum foil, it melts, puffs up, and burns with a luminous and smoky flame, leaving a cinder which it is very difficult to burn white. The latter is perfectly free from chlorine, and contains but a trace of sulphuric acid. A current of carbonic acid passed into the alcoholic solution of the hyocholate of soda does not render it turbid.

The pure salt, dried at 230°, was burnt with chromate of lead; it will be seen, from the following numbers, that the quantities of the constituents do not differ essentially from those of the impure salt after correction for the admixed substances. The material for analyses I., II., III., IV. were obtained from the bile by the above-mentioned process, but at different times. V. is of the salt prepared by saturating free hyocholic acid with carbonate of soda, evaporating the solution, extracting the salt from the residue with absolute alcohol, and precipitating with æther:—

	I.	II.	III.	IV.	V.	H = 1.		
Carbon....	65·43	65·57	65·40	65·77	..	54	= 524	65·85
Hydrogen	8·90	8·98	9·03	9·01	..	43	43	8·74
Nitrogen ..	3·01	..	..	..	..	1	14	2·84
Oxygen ..	..	..	..	..	..	10	80	16·27
Soda.....	6·15	6·14	..	..	6·27	1	31	6·30

Hyocholate of Potash, $KO, C^{54}H^{43}NO^{10}$, is contained in small quantity, along with the hyocholate of soda, in the bile of the pig. To obtain it pure, the soda salt was decomposed with sulphuric acid, the precipitated hyocholic acid dissolved in dilute caustic potash, and the solution mixed with sulphate of potash and warmed. The salt now separates in flakes, at the same time with the excess of sulphate of potash; it is washed with a saturated solution of sulphate of potash, dried at 212°, and then dissolved in absolute alcohol, from

which it is precipitated by æther. The salt is a white amorphous mass, which, as long as it contains water and alcohol, melts in the water-bath, puffs up, and after drying can be pulverized when cold, and now no longer cakes together at 248°. It has the same taste as the soda salt; the analysis gave—

Carbon	63·73	63·61	54 =	324·0	63·76
Hydrogen.....	8·75	8·61	43	43·0	8·46
Nitrogen	..	..	1	14·0	
Oxygen.....	..	..	10	80·0	
Potash	9·22	..	1	47·1	9·27

Hyocholate of Ammonia, $NH^4O, C^{54}H^{43}NO^{10}$, is insoluble in concentrated solutions of ammoniacal salts, and consequently separates from the solution of hyocholate of soda and from pig's bile on the addition of an excess of carbonate of ammonia, chloride or sulphuret of ammonium; it forms a crystalline white powder, which dissolves on the application of heat, but again falls on cooling. This salt dissolves readily in water and in alcohol; from the latter solution it is precipitated by æther. On boiling the aqueous solution, it becomes turbid, disengages ammonia, and acquires an acid reaction. Subsequently an acid salt separates. On desiccation at 212°, a portion of the ammonia escapes, and the residue no longer dissolves in water. The salt can be dried without loss of ammonia over sulphuric acid; it gave on analysis—

Carbon	66·1	54 =	324	66·5
Hydrogen.....	9·6	47	47	9·6
Nitrogen	5·1	2	28	5·8
Oxygen	..	11	88	

Hyocholate of Baryta, $BaO, C^{54}H^{43}NO^{10}$, is precipitated on the addition of chloride of barium to the solution of the preceding salt, or to the bile itself, in a gelatinous state. The salt is somewhat soluble in cold, more readily so in hot water, and still more so in alcohol; it has the same bitter taste as the preceding compounds, melts when heated, puffs up, and leaves a residue of carbonate of baryta, which it is extremely difficult to burn white. It was dried at 230°, and burnt with chromate of lead, when it afforded—

Carbon	59·66	59·66	..	54	324·0	60·29
Hydrogen	8·04	8·04	..	43	43·0	7·99
Nitrogen	..	..	..	1	14·0	
Oxygen	..	..	..	10	80·0	
Baryta.....	14·09	14·05	14·00	1	46·4	14·21

Hyocholate of Lime, $CaO, C^{54}H^{43}NO^{10}$.—When the bile precipitated from the alcoholic solution by æther is dissolved in water, and a dilute solution of chloride of calcium very cautiously added, there falls at first a perfectly white lime salt, which is collected on a filter. It dissolves in water more readily than the baryta salt, but is still precipitated from its solution in alcohol by æther. The alcoholic solution is precipitated by a current of carbonic acid. The following are the analytical results:—

Carbon	65·56	65·83	..	54 =	324	66·26
Hydrogen.....	8·79	8·87	..	43	43	8·79
Nitrogen	..	..	3·24	1	14	2·86
Oxygen.....	..	..	..	10	80	16·37
Lime.....	5·75	5·81	..	1	28	5·72

Hyocholate of Lead.—Pig's bile is precipitated by acetate of lead in the same manner as a solution of hyocholate of soda. The liquid filtered from the precipitate has an acid reaction; basic acetate of lead or ammonia produces a further precipitate in it, and a portion of the precipitate formed remains dissolved in the liquid; in fact, pig's bile behaves precisely like ox-bile towards salts of lead. The precipitate, which separates without the addition of ammonia, becomes flocculent on boiling, may easily be washed, and falls to a white powder on drying. The hyocholate of lead is somewhat soluble in water, dissolves readily in alcohol, and is precipitated from this solution by æther. The alcoholic solution turns reddened litmus-paper blue. The amount of oxide of lead in the salt varied between 23·1 and 24·4 per cent., which points to a basic salt, as the neutral salt should contain 19·5.

Hyocholate of Silver, AgO, C^{54} H^{43} NO^{10}, separates on mixing an aqueous solution of hyocholate of soda with one of nitrate of silver, as a gelatinous precipitate, which becomes flocculent on boiling. If an excess of nitrate of silver be avoided, the precipitate keeps perfectly white if washed and dried in the dark. It dissolves readily in alcohol, sparingly in cold, somewhat more in hot water. Analysis led to the following results:—

Carbon.....	56·40	55·87	54 =	324	56·15
Hydrogen	7·70	7·53	43	43	7·45
Nitrogen	..	..	1	14	
Oxygen	..	..	11	88	
Silver	18·44	18·78	1	108	18·72

Hyocholic Acid, C^{54} H^{43} NO^{10}, is obtained purest by precipitating a dilute aqueous solution of the pure soda salt with dilute sulphuric acid, dissolving in alcohol, and precipitating with water; the milky liquid, after long standing, deposits white drops. To obtain the liquid perfectly clear, it must be kept for several days on the warm sand-bath until the greater part of the alcohol has evaporated. The acid forms a white resinous mass, melts in water, and may then be drawn out into silky threads. So long as it is moist, it melts at 212°; it is very difficult to dry in the water-bath, can easily be pulverized when cold, and then remains solid at 248°. It is very sparingly soluble in water, somewhat more so in water containing acid, and dissolves readily in moderately-concentrated nitric or sulphuric acid; when moistened with water, it reddens blue litmus-paper. It dissolves readily in alcohol; the solution has an acid reaction. It is not quite insoluble in æther; it dissolves readily in solution of ammonia, and also in dilute solutions of the carbonated or caustic alkalies, no effervescence being perceptible with small quantities, from its weak saturating power; but on warming a moderate quantity of

the acid with a carbonated alkali, abundant bubbles of carbonic acid are disengaged. It yields the same purple colour as the other biles with sulphuric acid and sugar. 77·4 per cent. of acid were obtained by precipitating bile, purified with alcohol and æther, by muriatic acid; 1·502 grm. of bile, or after deducting the chloride of sodium 1·480, furnished 1·145 grm. of acid. Now since the bile contains 6·3 per cent. of soda, only 83·3 per cent. of the acid was obtained; the other 16·7 per cent. remained dissolved in the excess of muriatic acid and wash-water. The acid is very difficult to obtain perfectly pure, so as to leave no ash; it must therefore be repeatedly dissolved in alcohol, some muriatic acid added to it, and precipitated by water. On combustion with chromate of lead, it afforded—

Carbon	69·95	70·18	70·22	69·95	54	= 324	70·28
Hydrogen ..	9·63	9·81	9·57	9·60	43	43	9·33
Nitrogen ..	3·54	..	..	..	1	14	3·04
Oxygen	16·88	..	..	..	10	80	17·35

Products of Decomposition of Hyocholic Acid.—The acid combined with soda in the pig's bile is very constant. Boiling solution of caustic potash does not act upon it until it has been nearly concentrated to the state of hydrate, when it expels some ammonia. Dilute sulphuric acid, even with the assistance of peroxide of lead, does not exert any action. When fuming nitric acid is poured over it, heat is evolved and red fumes given off, but no further action is observed on keeping the substances cool. The mucus of pig's bile soon putrefies when the bile is kept in open vessels; but the acid of such a bile was still unaltered after three months.

Cholesteric Acid.—On distilling hyocholic acid, or one of its salts, with fuming nitric acid, and pouring back the distillate into the retort until no further action of the nitric acid is perceived by the appearance of red fumes, the residue is found to contain oxalic acid and cholesteric acid, which Redtenbacher obtained in the treatment of cholesterine and choloidic acid, and Schlieper likewise from cholic acid and nitric acid. The authors saturated the acid with lime, and precipitated from the solution of the purified lime salt, with nitrate of silver, yellowish flakes of cholesterate of silver, which dissolved on boiling with the addition of nitrate of ammonia, and again separated on cooling in yellowish masses. The substance, dried at 212°, afforded on analysis—

Carbon	24·1	8 =	48	24·0
Hydrogen.....	2·4	4	4	2·0
Oxygen.....	..	4	32	16·0
Oxide of silver.....	57·7	1	116	58·0

Hyocholic acid accordingly yields, on its oxidation with nitric acid, nearly the same products as choloidic acid; but no body having a resemblance to the choloidanic acid discovered by Redtenbacher was obtained.

On partially saturating with potash the product which distilled over in the action of nitric acid upon hyocholic acid, and rectifying, drops of oil passed over with the water, in which they sank. The

distillate, and especially the oil, possessed an odour which produced headache and faintness. The subsequent distillate smelt of volatile fatty acids, and contained a small quantity of a substance which appeared to be benzoic acid. The heavy oil, after being washed with water and placed in contact with potash, deposited crystals which bore a great resemblance to nitrocholate of potash. The volatile fatty acids were separated from the aqueous liquid by means of æther. The quantity sufficed to show at least by analysis that the carbohydrogens of the mixture, evidently of several acids, belonged to the formula $C^n H^n$.

Chromic acid, in the form of a mixture of bichromate of potash and sulphuric acid, likewise produces fatty acids, which are obtained on distillation along with a product of very disagreeable odour, and containing much prussic acid.—Liebig's *Annalen*, lxii. p. 205.

On a new Process for manufacturing Sulphuric Acid. *By* M. Schneider.

The author states, in a short notice, that he has succeeded in converting sulphurous acid directly into sulphuric acid by means of a porous body, for instance pumice-stone, and that this process may be employed for manufacturing sulphuric acid of 66° Beaumé without the necessity of leaden chambers or platinum retorts.—*Comptes Rendus*, xxv. p. 931.

ANALYTICAL CHEMISTRY.

On the Separation of Nickel and Cobalt. *By* Prof. Liebig.

Prof. H. Rose has recently described a method for the separation of nickel from cobalt*, which in accuracy and ease of execution surpasses all hitherto in use. In many cases the following may perhaps be employed with advantage.

The mixture of the two oxides to be separated quantitatively is treated with prussic acid, and then with potash, and heated until the whole is dissolved. Pure cyanide of potassium, free from cyanate of potash, may naturally be used for the same purpose. The solution is reddish-yellow; it is heated to boiling to expel the free prussic acid, when the protocyanide of cobalt compound is converted, with evolution of hydrogen, into cobalticyanide of potassium, and the nickel is contained in the solution as nickelocyanide of potassium. Now when pure powdered peroxide of mercury is added to the hot solution, the whole of the nickel is precipitated partly as oxide and partly as protocyanide, and the mercury takes the place of the nickel. If the liquid was neutral previous to the addition of peroxide of mercury, it becomes alkaline after boiling with this oxide.

* Chem. Gaz., vol. v. p. 362.

The precipitate which is formed is at first greenish; with an excess of the peroxide of mercury it assumes a dirty grayish-yellow colour. It contains the whole of the nickel, and moreover the excess of the peroxide of mercury. After washing and ignition, pure oxide of nickel, perfectly free from cobalt, remains.

The liquid which has been treated with the peroxide of mercury contains the whole of the cobalt in the form of cobalticyanide of potassium; to determine the amount of cobalt, the liquid is supersaturated with acetic acid and precipitated with a solution of sulphate of copper. This is effected while boiling, and the precipitate retained for a time in the liquid in ebullition; otherwise it contains potash, and continues mucilaginous, which prevents its being washed. The precipitate is cobalticyanide of copper, and contains 2 equivs. cobalt to 3 equivs. copper. On treating it with potash, oxide of copper is precipitated, while cobalticyanide of potassium remains in solution; and from the amount of oxide of copper the quantity of cobalt may be indirectly determined.

If it be desired to determine the cobalt directly, the precipitate is heated to redness, and after the destruction of the cyanogen, dissolved in muriatic acid with the addition of a few drops of nitric acid. A current of sulphuretted hydrogen is passed through the solution to remove the copper; and now, after boiling it for a few minutes to expel the sulphuretted hydrogen, the cobalt thrown down by a boiling solution of potash. The precipitate of the protoxide of cobalt must be well washed to remove the potash; after drying, it is heated to redness and weighed, and from a portion of the ignited oxide the cobalt determined by reduction with hydrogen, and calculated for the entire amount. All these operations can be effected with the greatest ease and without any loss.

It need not be stated, that the method is very much simplified by taking the weight of the two oxides or of the metals reduced by hydrogen, and determining only the amount of nickel. The tedious operations requisite for the quantitative determination of the cobalt are then avoided.

In confirmation of the correctness of the method, the author enumerates several determinations made according to this method; thus, in an analysis of the nickelocyanide of potassium, M. Lehmann found for the crystallized salt 22·62, and for the anhydrous salt 24·65 per cent. nickel, while the calculated quantities are respectively 22·54 and 24·49. In determining the amount of cobalticyanide of potassium, he obtained from 100 grms. 17·07 grms. of cobalt; theory gives 17·9. In another analysis he obtained 17·20. From a mixture of cobalt and nickel, M. Lehmann obtained, cobalt 48·47, nickel 50·24, the quantities taken being respectively 49·45 and 50·55.

The indirect determination of the cobalt from the amount of copper in the copper precipitate, appears to afford equally accurate results. M. Lehmann obtained from 1·040 grm. of the copper precipitate, dried at 212°, 0·337 oxide of copper, corresponding to 0·269 grm. copper, or in 100 parts—

	Calculated.	Found.
3 equivs. copper.....	25·51	25·87
2 equivs. cobalt.....	15·80	16·02

It will readily be perceived that the error in the determination of the cobalt is far greater than in that of the nickel, which is probably partly owing to the atomic weight of cobalt being somewhat lower than has hitherto been supposed. I do not think that any other method can surpass the one now described in accuracy and ease of execution. The cobalticyanide of potassium, purified by means of peroxide of mercury, is nearly white in small crystals, faint yellowish in large. The cobalticyanide of ammonium is perfectly colourless in large crystals. In the oxide of nickel precipitated by the peroxide of mercury not a trace of cobalt can be detected by means of the blowpipe.

When a mixture of the oxides of nickel and cobalt is mixed with prussic acid, and then with ammonia, and heated to boiling, cobalticyanide of ammonium and nickelocyanide of ammonium are obtained. If sulphuret of ammonium and sulphur are added to this solution, a dark black liquid is formed, which after long boiling becomes perfectly clear and colourless, while sulphuret of nickel subsides. The filtered liquid is perfectly free from nickel; but it now contains, besides the cobalticyanide, sulphocyanide of ammonium. This method is perhaps applicable in many cases, but I have not yet sufficient proof of its correctness.

With regard to the reduction of the cobalt from the oxide by hydrogen, I may observe that the metal, after cooling in the current of hydrogen, cannot be exposed to the air without taking fire; a trace of nickel deprives the cobalt of this inflammability.—Liebig's *Annalen*, Feb. 1848.

PATENT.

Patent granted to Richard Albert Tilghman, *for Improvements in the Manufacture of certain Alkaline Salts.*

This invention consists in certain methods of obtaining sulphate, muriate and chromate of potash from the felspars containing that alkali. The felspars which may be most advantageously treated, according to this invention, are those containing the largest quantity of potash; and the proportions of materials hereafter mentioned are calculated for a felspar containing 16 per cent. of potash.

To produce sulphate of potash, a mixture is made of 2 parts by weight of felspar, 1 part of lime, or an equivalent quantity of carbonate of lime, and 1 part of sulphate of lime (or sulphate of baryta or strontia, but sulphate of lime is preferred), all previously ground to fine powder; and this mixture is placed on the hearth of a reverberatory furnace, and kept at a bright red heat for about eight hours, the charge being turned from time to time, so that all parts may be equally heated. Although the formation of sulphate of potash is

most rapid at a high temperature, yet the heat must not be allowed to increase to such an extent as to cause the fusion of the mass, for the subsequent extraction of the salt by water will be thereby rendered more difficult; and as the presence of the deoxidizing atmosphere in the furnace is injurious to the formation of the sulphate, a sufficient quantity of air is admitted (through openings above the level of the fire) into the gases rising from the fuel to keep the atmosphere in an oxidizing state. The charge is withdrawn from the furnace at the expiration of about eight hours; it is then lixiviated with hot water repeatedly (as some of the salt adheres obstinately to the sulphate of lime); and the solution of sulphate of potash thus obtained is evaporated, the sulphate of lime which is precipitated during the evaporation being continually removed. If a cheap and abundant supply of sulphurous acid gas can be obtained, the use of sulphate of lime, or other sulphate, may be dispensed with, by doubling the quantity of lime or carbonate of lime, and exposing the charge, while at a red heat, to a current of sulphurous acid gas and air (frequently stirring the charge); by which means sulphate of lime is formed during the process, and sulphate of potash is produced, as before.

Muriate of potash is obtained by heating a potash felspar with muriate of soda, lime or iron, at a temperature above the fusing-point of the muriate employed. The patentee prefers to use muriate of soda, which he mixes with an equal weight of finely-ground felspar; the mixture is well dried, and introduced into a horizontal iron cylinder, covered on the outside with fire-brick, to protect it from the action of the fire, and having an opening only at one end, which is closed with an iron door and luted tight; and to permit the escape of any gas that might be likely to burst the cylinder, a small hole is made in the upper part of the door, which may be closed by a loosely-fitting plug. The cylinder and its contents are kept at a bright red heat for about six hours; the cover is then taken off, and the charge raked out as quickly as possible into an iron pot, which is immediately covered and kept closed until the mass is cool; after which it is lixiviated with water, to extract the soluble salts; and the muriate of potash is separated from the other salt by evaporation and crystallization.

Chromate of potash is obtained by the following process:—4 parts by weight of felspar, 4 parts of lime, or an equivalent quantity of carbonate of lime, and 1 part of chrome ore, all in fine powder, are mixed together, and kept at a bright red heat, in a reverberatory furnace, for from eighteen to twenty hours, the mixture being turned over frequently, so that all parts may be equally exposed to heat and air. An oxidizing atmosphere is maintained by the admission of sufficient air into the chamber of the furnace; and the heat is not permitted to rise high enough to cause even incipient fusion in the charge, which should be kept in a porous state. When the charge, on being examined in the ordinary way, is found to contain the proper quantity of alkaline chromate, it is withdrawn from the furnace and lixiviated with water.—Sealed Feb. 1, 1847.

THE CHEMICAL GAZETTE.

No. CXXXII.—April 15, 1848.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Examination of the Bile of the Ox. By A. Strecker.

The investigations of the bile hitherto made, excepting those quite recent, have been almost entirely confined to the bile of the ox. Strecker and Gundelach have lately carefully studied the bile of the pig *, and the simplicity of the results obtained by these chemists led us to hope that they would conduce to a further and more general knowledge of this substance. How great the doubts regarding the true nature of the bile have become, in consequence of the conflicting views of the chemists of the present day, is well known. Strecker, in his researches on the biliary fluids, has also resumed the study of the bile of the ox, and arrived at a result which allows of our viewing the facts in a more simple serial order than before. From what follows, the bile consists essentially of the soda-salt of a nitrogenous acid, free from sulphur (Gmelin's cholic acid), and a substance which contains all the sulphur of the bile, and is decomposed by acids into a resin, taurine and ammonia.

1. *Crystallized Bile.*—Ox-bile which had been previously dried in a water-bath and then in an oil-bath at 212°, was dissolved in cold absolute alcohol, and without decolorizing the solution, treated with some æther. After having been set aside for a considerable time, the syrupy dark-coloured mass which subsided separated into crystals and an amorphous matter. The clear supernatant liquid was poured into a dry glass, and again treated with æther, whereupon, after considerable repose, a further quantity of white or pale yellow needles subsided, the amount of which was considerably increased by the gradual addition of æther.

The crystals were transferred to a filter by means of alcohol containing one-tenth part of æther, with which they were washed. They are but slightly soluble in this menstruum. They were then dried for twenty-four hours over sulphuric acid, after which they no longer effloresced on exposure to the air. If exposed to the air while still containing æther, they absorb water and deliquesce. The crystals contain but very little chloride of sodium. On the combustion of the substances obtained by four separate preparations and dried at 212°, the crystals yielded 60·5–60·6 per cent. of carbon and 8·63–8·67 per cent. of hydrogen. However, the quantity of ash was not constant,

* Chem. Gaz. p. 138 of the present volume.

varying between 14·0 and 15·1 parts of sulphates, which remained after moistening with sulphuric acid and heating to redness 100 parts of the crystals, and contained traces only of potash. The quantity of sulphur, which was determined by fusion with nitre and hydrate of potash, amounted to 2·5–2·7 per cent. The nitrogen amounted to 2·8 per cent. The precipitate, which was produced by the addition of chloride of platinum to an alcoholic solution of the crystals, contained potash as well as a little ammonia. An aqueous solution was almost completely precipitated by basic acetate of lead; and on decomposing the lead-salt with carbonate of soda, potash or ammonia, the crystals could be again obtained by the addition of æther to the solution of the mass obtained on evaporation to dryness in absolute alcohol. They contained the same amount of sulphur, 2·6 per cent., and now the quantity of base they contained was constant.

2. *Cholic Acid.*—The crystals, moist from containing alcohol and æther, were dissolved in water, and decomposed by dilute sulphuric acid. After twelve hours, colourless crystals had formed, and an oily substance separated in drops. They were washed with cold water, when the oily drops dissolved. The turbid wash-water deposited a resinous precipitate after some days. The crystals were now snow-white. The precipitate which separated on the addition of sulphuric acid to the bile, purified by Theyer and Schlosser's method, on the addition of æther was converted into a network of the same crystals. Berzelius states, that by this process he did not obtain any crystals, but a syrupy mass consisting of bilifellinic acid and biline, whilst fellinic and cholinic acids remained dissolved in the æther. The crystals were dissolved in boiling water, in which the greater part was dissolved, and on cooling, again crystallized. They now had all the properties of Gmelin's cholic acid. They formed delicate needles, in which no diameter could be perceived even when magnified 300 times linear. 1000 parts of boiling water dissolve 8·3 and cold water 3·3 parts of the acid. Its cold solution in water tastes sweet and somewhat bitter, reddens litmus, and yields no reaction with acids, acetate of lead, bichloride of mercury, or nitrate of silver. Basic acetate of lead produces a slight precipitate. It is readily soluble in alcohol, and after the evaporation of the latter remains as a resinoid syrupy mass. It has been already noticed by Plattner, that this causes the acid to undergo a change. When the alcoholic solution is mixed with water, it may be filtered without anything remaining on the filter. In twelve hours acicular crystals form; if the acid was pure, the supernatant liquid is colourless. The acid is little soluble in æther, but a very large quantity of æther is required to precipitate it even from concentrated alcoholic solutions. In æther containing but little alcohol it dissolves copiously, and remains in crystals after the spontaneous evaporation of the fluid. It is copiously dissolved by cold concentrated sulphuric, muriatic and acetic acids; and on the evaporation of the latter at a gentle heat, remains in the form of crystals. On heating the solution in concentrated mineral acids, oily drops separate. The acid dissolves in large quantity in aqueous solution of ammonia, dilute

solution of potash and soda, and also in barytic water. On the addition of acids, a resinoid precipitate falls, which, when set aside for a considerable time, is converted into crystals resembling wavellite. The acid, as also its salts, pass more readily into the crystalline state when æther is added. Its neutral salts, when dissolved in water, yield no precipitate with those of the alkaline earths. Acetate of lead produces a precipitate, and the basic acetate causes another slight precipitate in the filtered fluid. The fluid filtered from this still contains a little oleic acid. Salts of copper produce bluish-white and chloride of iron yellow flakes, which dissolve in alcohol. Nitrate of silver causes a copious gelatinous precipitate in a solution which contains 1 per cent. of cholic acid; this is partly dissolved on ebullition, and separates, when slowly cooled, in crystals; when rapidly so, in an amorphous state. The precipitate becomes coloured by exposure to the light, but little so in the dark, even on boiling.

3. *Paracholic Acid.*—When cholic acid is boiled for a considerable time with water, it is transformed into insoluble paracholic acid, no more crystals subsequently separate from the filtered water, and fragments of six-sided tables remain upon the filter. The same crystals could also be distinguished under the microscope among the capillary crystals of the cholic acid crystallized from water. Except the insolubility in water, they have all the properties of cholic acid, and when dissolved in alcohol and precipitated from it by water, are reconverted into cholic acid; they then separate in acicular crystals, which are now soluble in hot water. Thus, by recrystallization from water, cholic acid is partly converted into paracholic acid, and on recrystallization from alcohol the latter is converted into cholic acid. On analysis, no difference was found in the composition of these two substances. Nor could any difference be detected in the salts of the two acids. On decomposing the paracholates with acids, a mixture of the two acids is constantly precipitated.

If fresh bile is directly decomposed with sulphuric acid, and after removing the supernatant fluid and washing the precipitate itself with dilute sulphuric acid, æther is added to the latter, a large quantity of white stellate crystals form in the coloured precipitate. If fresh bile be immediately precipitated with solution of acetate of lead, and the yellowish precipitate, after being well washed, be dissolved in boiling alcohol of 0·848 spec. grav., which partly takes it up, and the lead be separated by sulphuretted hydrogen from the yellowish solution, which is filtered whilst hot, on the addition of water to the alcoholic solution in air-tight closed vessels, in twelve hours a large quantity of a mixture of cholic and paracholic acids is obtained. This method is more convenient than that of obtaining it from crystallized bile. 13·5 grms. of cholic and paracholic acids were obtained from ten gall-bladders. The fluid, poured off from the crystals with the wash-waters, on exposure to the air deposits tolerably large quantities of the acids, which may be obtained by the very careful evaporation of the fluids. At last a very minute resinoid residue is left. Berzelius decomposed the lead precipitate, mixed

with alcohol, by sulphuretted hydrogen, and evaporated the alcoholic solution; he considered the brown resinoid residue to be cholinic acid. Since cholic acid on evaporation is converted into a resinous substance, this is readily explained.

These latter experiments show that the cholic acid exists already formed in the fresh bile of the ox. The precipitate with acetate of lead consists principally of cholate of lead. In the fluid filtered from the latter precipitate, basic acetate of lead also produces a precipitate, which is more or less coherent, and also contains cholic acid; however, it yields less. Cholic and paracholic acids exhibit the reaction of Pettenkofer's test for bile with sulphuric acid and sugar in a great degree. The sugar may, in this case, be replaced by acetic acid. The weight of cholic acid and paracholic acid, which has been dried at 212° F., remains unchanged even at 266° F. Both acids are free from sulphur. The results of the analysis of the acids, dried at 212° F., are subjoined:—

	Cholic acid.						Paracholic acid.		
Carbon....	67·31	67·26	66·97	66·88	67·07	66·80	67·18	67·40	67·31
Hydrogen..	9·35	8·36	9·38	9·22	9·35	9·28	9·24	9·29	9·32
Nitrogen ..	3·23	..	..	..	..	..	2·73		
Oxygen ..	20·11	..	..	..	..	..	20·85		
	100·00						100·00		

These numbers, in the case of both acids, with the atomic weight found from the barytic salt, lead to the formula $C^{52}H^{42}NO^{12}$, and in their salts $C^{52}H^{42}NO^{11}$. In the precipitate thrown down from ox-bile by acetate of lead, which was purified by solution in alcohol, Mulder found the acid contained in it to be of the same composition; he gave it the formula $C^{52}H^{42}NO^{12}$. In consequence of Mulder having subsequently found 1·67 per cent. of sulphur present, and considered it as essential, he assigned to it the formula $C^{102}H^{86}N^{2}O^{21}S^{1}$.

Cholate of Soda.—Cholic acid is readily soluble in dilute solution of soda. The soda-salt separates in an amorphous form from the concentrated ley, or on the addition of carbonate of soda. To obtain the cholate of soda, cholic acid was dissolved in solution of carbonate of soda, and the neutral solution evaporated to dryness; or an alcoholic solution of cholic acid was shaken with effloresced carbonate of soda, and the alcohol evaporated. The dry residue was then dissolved in absolute alcohol, and the solution treated with æther; in a short time the soda-salt separated in white needles grouped in a stellate manner, and exactly resembling those of the crystallized bile. 1000 parts of absolute alcohol at 59° dissolve 39 parts of cholate of soda. When the alcohol is rapidly evaporated, the salt remains in the amorphous form. When heated, the salt melts, burns with a smoky flame, and leaves an ash, which is alkaline, readily fusible, and contains cyanogen. The crystals, dried at 212°, yielded—

						Calculated.	
Carbon	63·85	63·78	..	..	..	52	=64·06
Hydrogen	8·71	8·77	..	..	..	42	8·62
Nitrogen	..	..	..	..	..	1	2·87
Oxygen	..	..	..	..	..	11	18·09
Soda	..	..	6·14	6·16	6·21	1	6·36
							100·00

The amount of carbon and hydrogen contained in this substance is far greater than that in the whole bile as thrown down from the alcoholic solution of the bile by æther, which Theyer and Schlosser found to contain 57·7 per cent. of carbon and 8·3 per cent. of hydrogen. It must therefore, in addition to cholate of soda, contain a substance which is poorer in carbon and hydrogen. The nitrogen in this substance, from Theyer and Schlosser's experiments, would amount to rather more than 3 per cent., which is the same quantity as in cholic acid. The amount of soda also in this second constituent of the bile containing sulphur, which is spoken of more in detail below, can be but slightly, or not at all, different from that of the cholate of soda. 6·3 per cent. may be considered as the mean of all the analyses of the so-called bilate of soda.

Cholate of Ammonia is formed on passing dry ammonia into the solution of cholic acid in absolute alcohol, or what is better, alcohol mixed with æther. The ammonia should not be passed through so long as to produce a precipitate. The salt forms crystals, which are exactly like those of the soda-salt. They are readily soluble in water, and on ebullition give off ammonia. When dried *in vacuo* they also lose ammonia, and then acquire a slightly acid reaction. The amount of nitrogen, when calculated for the formula $C^{52}H^{42}NO^{11}NH^{4}O$, amounts to 5·8 per cent. The quantity found was 5·4.

Cholate of Potash resembles the soda- and ammonia-salts in every respect.

Cholate of Baryta.—Cholic acid is dissolved in barytic water, and carbonic acid passed through the solution; this does not decompose the barytic salt; the mixture is heated, filtered from the carbonate of baryta, and evaporated to dryness. The salt remains in an amorphous state. It is not obtained in crystals even on the evaporation of its alcoholic solution, from which also carbonic acid does not throw down any baryta. The aqueous solution has a powerfully sweet taste, with but slight bitterness. 1000 parts of water at 59° dissolve 162 parts of the barytic salt. It dissolves with more difficulty in absolute alcohol than in water. The following numbers were obtained on the analysis of the salt dried at 212°:—

Carbon	58·43	58·21	58·17	52	=58·60
Hydrogen	8·00	8·10	8·07	42	7·88
Nitrogen	..	..	..	1	2·63
Oxygen	..	..	..	11	16·54
Baryta (separate determinations)	14·31	14·41	14·34	1	14·35
					100·00

The cholic acid treated of here (containing nitrogen) is identical with that of Gmelin, and different from that (free from nitrogen) of Berzelius. Strecker's cholic acid, when boiled with concentrated acids, yields resinous acids containing nitrogen. After boiling with muriatic acid for twelve hours, the residue is insoluble in alcohol, and hence resembles dyslysine. On ebullition with alkalies, ammonia and a carbonaceous substance gradually escape, and an acid, free from nitrogen, remains in the residue, which is identical with Demarçay's cholic acid. Strecker calls the latter acid cholalic acid. The reason of Berzelius not having been able to obtain this acid by boiling biline with potash is because it is formed from Gmelin's cholic acid.

4. *The Constituent containing Sulphur.*—From what has been said, it appears evident that cholate of soda is a principal constituent of the bile; and in connexion with former researches on the bile, that it must also contain a substance which contains all the sulphur of the bile, and which on its decomposition yields a resin, taurine and ammonia. The author is still engaged in the investigation of this remarkable substance, but at present he states as follows:—It appears that this body does not crystallize. It dissolves fats, fatty acids and cholesterine in considerable quantity; and its presence is the cause of the cholic acid in the ox-bile not being precipitated by acetic or dilute mineral acids. If a little of this substance be added to the solution of a pure alkaline cholate, a precipitate is no longer produced on the addition of acids. Only when considerable quantities of sulphuric acid are added is a resinous matter precipitated, which however carries down the sulphuretted body with it whether decomposed or not. This property of the sulphuretted substance (picromel, biliary sugar, biline) was stated by Thenard, and subsequently by Gmelin, and both explained the solution of the biliary resin in the bile of the ox by it. The readiness with which it is decomposed renders it difficult to be obtained; according to Berzelius, the substance (biline) is decomposed even on the evaporation of its aqueous solution.

Views on the Composition of the Bile.—According to Berzelius,—1st, pure bile, freed from fat and colouring matter, consists principally of biline; 2nd, this is decomposed with extreme facility, and when acids are present produces fellinic and cholinic acids, ammonia and taurine; 3rd, the precipitate produced in the bile by salts of lead is bilifellinate and bilicholinate of lead; 4th, when this precipitation occurs, biline remains in solution; 5th, bilifellinic and bilicholinic acids are formed from the metamorphosis of the biline, taurine being the principal secondary product of its decomposition. Mulder adopts essentially the same views. He considers that all the acids, when not combined with ammonia and biline, are free from nitrogen.

According to Strecker,—1st, this biline does not exist, because from the bile of five fresh gall-bladders, which left 29 grms. of dry residue, in following the process given for obtaining the biline, he obtained in one experiment only 2 per cent., in another only 1·4 per

cent. of the dried bile of a substance which still contained ash. As regards the points 2, 3, 4 and 5, Strecker first refers to the experiments of Theyer and Schlosser, according to which the precipitate produced in the bile by salts of lead only contains an organic substance, which is identical with the organic substance of the bile combined with soda, whilst, on the one hand, the body remaining in solution on this precipitation (Biline, *Berz.*) has exactly the same composition as that precipitated, and on the other hand, taurine could not be found either in the precipitate or in the solution. He further adds, that he obtained the same *crystallized* bile from that portion of the bile which is not precipitated by lead as he obtained immediately from the fresh bile. Bile was precipitated by basic acetate of lead and ammonia. The lead was removed from the solution by sulphuretted hydrogen, and the liquid after filtration concentrated and treated with concentrated solution of soda. The soda-salt which separated was washed with solution of soda, and then dissolved in absolute alcohol. After passing carbonic acid through, the excess of soda was separated by filtering it off as carbonate after the alcoholic solution had stood for some time. On the addition of æther, crystals of reproduced crystallized bile soon separated. Hence biline is nothing more than bile, the precipitation of which by salts of lead is prevented by the acetate of ammonia and soda formed.

The substance of Strecker's view of the constitution of the bile then comes to this;—that the bile, in addition to the soda-salt of the nitrogenous cholic acid, which is free from sulphur, also contains the soda-salt of a sulphuretted choleic acid free from nitrogen. Thus the first precipitate produced in the bile by acetate of lead contains the cholic acid; that subsequently precipitated by basic acetate of lead he finds essentially different from the first; it is a mixture of cholate of lead with the lead salt of the sulphuretted acid. If the two acids be supposed to exist ready-formed in the bile, the reaction of the bile may be readily explained. Thus, as stated above, the sulphuretted substance (choleic acid containing sulphur) separately is not precipitated by acids, and moreover the precipitation of the cholic acid mixed with it is prevented; this explains, *e. g.* the reaction of acids upon the bile. If, in a mixture of the two acids, the sulphuretted acid is diminished, on the addition of acids it is precipitated with the insoluble cholic acid; in fact, in this case, crystallized bile is precipitated by acetic acid. If the cholic acid predominates greatly, it immediately takes up the sulphuretted choleic acid, for the substances precipitated by acids in this case contain sulphur.

Every kind of bile, according to Strecker, is a mixture of a nitrogenous acid free from sulphur and a sulphuretted acid free from nitrogen. From the relative quantities of these, which remain almost constant in the same, but vary in different classes of animals, the almost uniform composition of the bile of the ox in different analyses may be explained, as also the difference of the latter, *e. g.* from the bile of the pig. The same differences are especially observed on the comparison of the bile of the *Boa anaconda*, which contains 6·3 per cent. of sulphur, with pig's bile, which is free from sulphur,

or contains but a very small quantity. The acid containing sulphur appears to be the same in all animals; at least, a product of its decomposition, taurine, has been found in every kind of bile except that of the pig, in which it is absent. On the other hand, the acid free from sulphur is different, even in the only two kinds of bile which have been examined in regard to this point. Cholic acid is $= C^{52} H^{43} NO^{12}$, hyocholic acid $= C^{54} H^{43} NO^{10}$. If 2 equivs. of water be subtracted from the composition of cholic acid, there remain $C^{52} H^{41} NO^{10}$, a formula which only differs from hyocholic acid by $C^2 H^2$, which is the same hydrocarbon as that causing the difference of the volatile fatty acids $C^n H^n O^4$. In fact, on boiling cholic acid with muriatic acid, these 2 atoms of water are set free, and a resinoid substance, bearing the greatest resemblance to hyocholic acid, remains.—*Ann. der Chem. und Pharm.*, vol. lxv. p. 1–37.

On the Disintegration of Rocks. By M. Ebelmen.

The following analyses A. are of a compact and disintegrated graystone from the district of St. Austell in Cornwall; the analyses B. are of basalt of a similar nature from the neighbourhood of Linz. The several constituents are expressed in their relation to 100 parts of alumina:—

	A. Compact.	A. Decomposed.	A. Decomposed.	B. Compact.	B. Decomposed.
Alumina	100	100	100	100·0	100·0
Silica	325	212	201	283·0	228·0
Lime	36	5	6	63·0	43·0
Magnesia	17	14	12	39·0	29·0
Peroxide of iron	106	107	79	80·0	78·0
Oxide of manganese	3	2			
Oxide of titanium	4	4	4	6·0	6·0
Potash	10	14	13	7·4	2·6
Soda	23			22·2	7·4
Water	11	43	38	15·0	35·0
	631	497	449	615·6	529·0

From these numbers it is seen that the alkali, and in certain cases the silica, lime, magnesia and peroxide of iron, have a tendency to separate from the constitution of the rock. Of all the constituents, water is the only one which occurs in larger quantity in the decomposed than in the undecomposed mineral. The product resulting from the disintegration approaches more and more to the state of a hydrated silicate of alumina, results which agree perfectly with the author's former experiments, and from which are drawn the following two conclusions:—1. Silicates which contain no alumina lose on disintegration silica, lime and magnesia. The iron sometimes disappears with the other bases, and sometimes remains in the residue as peroxide of iron. In the first case nothing is left of the entire

silicate. 2. The silicates containing alumina and an alkali, or likewise other bases at the same time, become more rich in alumina on disintegration; this alumina retains the silicic acid, and assimilates water, while the other bases with a portion of the silicic acid disappear. In this case the residue approaches in composition to a hydrated silicate of alumina.

Nearly all rocks of igneous origin contain alumina, and consequently leave a clayey residue on their decay. The clay of the stratified rocks must undoubtedly have been derived from the primitive rocks, upon the decomposition of which it was carried away.

The different bases which are eliminated from any rock of igneous origin must deprive the atmosphere of a considerable amount of oxygen and carbonic acid. In fact, a stratum of very small extent of decomposed plutonic rocks is sufficient to deprive the atmosphere of the whole of the carbonic acid contained in it. At the same time, the stratified clays point to the decomposition of immense masses of plutonic rocks, and likewise to the absorption of a far greater amount of carbonic acid than at present exists in the atmosphere. This amount of carbonic acid may however have been gradually absorbed from the atmosphere, without the air having possessed a different composition during the several geological epochs than at present. The author regards volcanos as the principal sources which replace the loss of carbonic acid sustained by the atmosphere in saturating the bases set free during the decay of plutonic rocks. The well-known fact, that even extinct volcanos still give off considerable quantities of carbonic acid, in connexion with the phænomenon that the carbonic acid is again fixed by the decomposed rocks of igneous origin, is particularly interesting, since the igneous state of the nucleus of the earth appears essentially requisite for the preservation of life upon the earth's surface. The equalization of the loss of carbonic acid by vegetation, which has been assumed since the time of De Saussure, has not sufficed to explain the uniform composition of the air, and the influence of the mineral kingdom must also be taken into consideration.—*Comptes Rendus*, xxvi. p. 38.

Notice respecting the Platino-cyanides. *By* B. Quadrat.

In the February number of Liebig's 'Annalen' the author observes, that his experiments on the platino-cyanides (Chem. Gaz. p. 109 of the present volume) had forced him to adopt the view of the existence of two series of platino-cyanides, the most simple of which correspond in composition to Gmelin's potash salt; the second and more complex contain for every 5 equivs. of the simple salt 1 equiv. of the metallic cyanide.

Improbable as this second series must appear to every chemist, and although his experiments were made more with a view to refute the existence of this second series, yet the remarkably accordant relations of composition in several salts compelled him to admit the second complex series.

He has recently found that the acid separated by means of sul-

phuretted hydrogen from the green precipitate obtained with sulphate of copper and Gmelin's potassium compound contains sulphur, and after saturation with a base colours salts of the peroxide of iron of a deep blood-red. Most of the salts obtained from it contain a sulpho-cyanide. When the green precipitate is treated with calcined magnesia or with barytic water, platino-cyanide of magnesium and platino-cyanide of barium are obtained, which are in constitution exactly proportional to the potassium compound.

When these salts have crystallized, the mother-ley contains salts the composition of which differs from that of the potassium compound; they are perfectly colourless and far more soluble in alcohol. The author states that he is now engaged in examining these salts*.

On some Phosphates of Lead. *By* C. Gerhardt.

In the analysis of the compounds containing phosphorus, it is sometimes requisite to separate the phosphoric acid by double decomposition as a salt of lead, and it is supposed that a neutral solution yields the tribasic phosphate of lead. According to my experiments, the phosphates of lead vary according to the nature and mass of the soluble salts of lead employed.

When an alkaline phosphate is poured into a boiling solution of chloride of lead, the latter being in excess, the crystalline precipitate contains $2PbO, HO, PO^5 + PbCl$. It is a chlorophosphate, insoluble in boiling water; at 212°, it parts with its water but very slowly. This compound may be formed whenever a phosphate is precipitated by a soluble salt of lead in the presence of a chloride.

The nitrate of lead affords a similar compound. When an alkaline phosphate is added to it, keeping the nitrate in excess, a crystalline precipitate results, insoluble in cold water, and represented by $3PbO, PO^5, PbO, NO^5 + Aq$. This nitrophosphate crystallizes from nitric acid in hexagonal tablets. Boiling water decomposes it into nitrate and tribasic phosphate, $3PbO, PO^5$, which is likewise obtained directly from the acetate, or when nitrate of lead is poured into an excess of the phosphate. These facts show that the phosphates of the alkalies behave towards salts of lead in the same manner as the alkaline oxides themselves; just as the latter yield, according to the proportions, either oxide, or chloride, or oxynitrate (subnitrate), or oxychloride, we likewise obtain with the phosphates either phosphate of lead or nitrophosphate or chlorophosphate. In fact, the subsalts are true double salts.

* In a note to this paper Prof. Liebig observes, that he has induced Dr. Baumert to submit to analysis one of the salts prepared according to the above method, when the following confirmatory results were obtained. The platino-cyanide of magnesium still contains at 230° 2 atoms of water; it is then white; dried at 392°, it is anhydrous and of a yellow colour. The per-centage results obtained agree for the salt dried at 392° with the formula $Pt\,Mg\,Cy^2$:—

Platinum	60·51	59·81	1 =	98·56	60·60
Magnesium	7·38	7·28	1	12·07	7·42
Cyanogen	...	...	2	52·00	31·98

The pyrophosphates behave in a very different manner, and their reactions with salts of lead readily distinguish them from the phosphates; they do not yield nitrophosphate with an excess of the nitrate; the flocculent precipitate constitutes a very pure pyrophosphate of lead, $2PbO, PO^5$.

If, instead of adding the pyrophosphate to an excess of the nitrate, the reverse is done, the precipitate redissolves at first whilst warm, and when it has subsequently become permanent, it contains variable quantities of the alkaline metal. A definite compound, NaO, PbO, PO^5, may be obtained in the form of a granular precipitate, insoluble in boiling water, by heating the solution of the first precipitate in pyrophosphate of soda to ebullition.—*Ann. de Chim. et de Phys.*, April 1, 1848.

On the Inorganic Constituents of the Berries of the Coffee Plant (Coffea Arabica). *By* Thornton J. Herapath, Esq.*

Having been desirous, some short time since, of determining the best manure for the West Indian coffee plantations, it became necessary for me, in the first place, to ascertain the composition of the inorganic constituents of the coffee berry. For this purpose 150 grs. of very fine West Indian coffee berries, which had been dried in a gas stove at a temperature of about 220° F., were taken, and carbonized at a gentle heat in a loosely-covered platinum crucible, as recommended by Prof. Rose†. The carbonaceous mass thus obtained was then repeatedly digested with boiling water, until a drop of the solution, when evaporated to dryness on a glass plate over a spirit-lamp, left only the slightest perceptible trace of residue; it was then dried and heated to redness in a large flat-bottomed platina dish, over an Argand burner, until all the carbon was consumed and a pure white ash remained behind. The ash thus obtained was very carefully transferred to a porcelain crucible containing a small lump of neutral carbonate of ammonia, and it was then subjected to a gentle heat, the top of the crucible having been previously imperfectly closed with a piece of platina foil. The soluble salts having been extracted from the ash by means of hot water, the solution was added to that from the charred mass, and the whole evaporated to dryness; the weight of the residue, which comprised the entire soluble salts, was 2·01 grs.

The salts insoluble in water, after having been dried and heated to dull redness, were found to weigh 2·94 grs.; which, when added to the weight of the soluble salts, gave 4·95 grs. as the total weight of the ash.

The process of analysis pursued in this investigation was similar to the one described by me in a paper "On the composition and distribution of the inorganic substances in the different organs and component organic parts of the mulberry-tree," recently communicated to the Chemical Society.

* Communicated by the Author.

† Chem. Gaz., vol. v. p. 158.

The soluble salts were found to contain—

Phosphoric acid	0·904	
Sulphuric acid	0·011	
Potash	0·755	
Soda	0·326	
Chlorine	0·018	
	2·014	
— excess of oxygen in soda	0·004	
		2·010

The insoluble salts contained—

Carbonic acid	0·381	
Sulphuric acid	0·047	
Phosphoric acid	0·960	
Lime	1·260	
Magnesia	0·272	
Silicic acid	0·020	
		2·940
		4·950

From these analyses it follows that the per-centage of ash is 3·3, and that 100 grs. of the ash contain of—

Phosphoric acid	18·273
Sulphuric acid	0·224
Potash	15·238
Soda	6·264
Chloride of sodium	0·606
Carbonate of lime	3·838
Carbonate of magnesia	11·515
Sulphate of lime	1·616
Phosphate of lime (tribasic)	42·022
Silicic acid	0·404
	100·000

Deducting the carbonic acid, we obtain the following per-centage composition:—

Phosphoric acid	19·801
Sulphuric acid	0·244
Potash	16·512
Soda	6·787
Chloride of sodium	0·645
Lime	2·329
Magnesia	5·942
Sulphate of lime	1·751
Phosphate of lime	45·551
Silicic acid	0·438
	100·000

And, consequently, for every ton of dried coffee berries that is raised on a plantation, the proprietor must consider about the fol-

lowing quantities of the various mineral substances as having been removed from his land:—

	lbs.	oz.
Phosphoric acid	27	14½
Sulphuric acid	0	13½
Potash	11	4
Soda	4	10
Chloride of sodium, or common salt	0	7
Lime	18	14
Magnesia	4	1
Silicic acid, or silica	0	5
	68	5

Mansion House, Old Park, Bristol,
April 5th, 1848.

On the Behaviour of Iodine towards the Oils of Aniseed and Fennel. *By* Dr. H. Will.

When a perfectly-saturated cold aqueous solution of iodide of potassium is mixed with so much iodine as it is capable of dissolving, and essential oil of aniseed or fennel added in drops to this dark brown solution of iodine under constant agitation, a thick gelatinous magma is formed, which, upon the addition of 6 to 8 times the volume of alcohol, deposits a pulverulent body, which becomes dazzling white by washing with alcohol. The oils of fennel and aniseed behave exactly alike towards the solution of iodine, as will be seen from the following analyses of the white substance. The oil of carraway, wormwood, camomile, tansy, rue, cloves, and peppermint, do not yield a similar solid substance when treated in the same manner.

The quantity of the white substance obtained from oils of fennel and aniseed is pretty considerable; it amounts to more than half of the oil employed. One quantitative experiment with oil of fennel afforded 3·44 grms. of the solid product from 6·10 grms. of the essential oil, or 54·8 per cent. In its pure state it is a dazzling white, amorphous, very light and highly-electrical powder. It melts at a higher temperature than 212°, and on cooling solidifies to a colourless vitreous mass, without a trace of crystallization. At a higher temperature it is completely volatile, diffusing the odour of the oil of aniseed even when it has been prepared from genuine oil of fennel. It is wholly insoluble in water and in alcohol of every strength; æther, on the contrary, dissolves it in considerable quantity; from this solution it is again precipitated by alcohol almost entirely, and with all its properties. Potash, ammonia, dilute sulphuric and muriatic acids have no action upon it even at the boiling-point; concentrated nitric acid decomposes it, but only when kept boiling for some time; concentrated sulphuric acid immediately colours it dark brownish-red, but only when boiled for a considerable length of time; it forms when heated a light brownish-red solution, which on dilution with water becomes colourless. At the ordinary temperature the powder becomes coloured violet by dry chlorine gas, evolving

heat with the absorption of chlorine and disengagement of muriatic gas, but without fusing; when the powder is previously heated to 212°, the violet colouring does not make its appearance. Muriatic gas has no action upon it. It is perfectly free from iodine; for its vapour, passed over incandescent caustic lime in a glass tube, did not, after dissolving the lime in dilute nitric acid, indicate the slightest reaction with nitrate of silver. Analysis led to the following numbers:—

	From oil of fennel.		From oil of aniseed.
Carbon	77·90	78·00	77·68	77·20
Hydrogen.....	..	8·20	8·48	8·49
Oxygen.....	..	13·80	13·84	14·31

These numbers correspond most closely to the following formulæ:—

	Equiv.		In 100 parts.	Equiv.		In 100 parts.
Carbon	30	= 180	78·2	30	= 180	77·99
Hydrogen....	18	18	7·8	19	19	8·22
Oxygen.....	4	32	13·9	4	32	13·79

Blanchet and Sell have advanced the formula $C^{10} H^{6} O$ for the stearoptene of the oils of fennel and aniseed; the above body would consequently be formed from the stearoptene of these oils by assuming that 3 atoms $= C^{30} H^{18} O^{3}$ have assimilated either 1 atom of oxygen according to the first formula, or 1 atom of water according to the second. The first supposition is the more probable, as the iodine evidently has an oxidizing action, transferring oxygen from the water to the stearoptene and forming hydriodic acid. The analysis of the compound obtained by acting with dry chlorine upon the white body supports this view. The chlorine was passed over the substance at 212° until no further increase in weight was perceptible, and the excess of chlorine was then expelled by a dry current of air. It afforded on analysis—

Carbon	52·7	30	= 54·0
Hydrogen	4·7	15	4·5
Chlorine	31·9	3	31·6
Oxygen	10·7	4	9·9

leading to the formula $C^{30} \left.\begin{matrix} H^{15} \\ Cl^{3} \end{matrix}\right\} O^{4}$, according to which 3 equivs. chlorine have replaced 3 equivs. hydrogen in the body $C^{30} H^{18} O^{4}$.

The loss in carbon is explained from the action of the chlorine having proceeded somewhat too far. A second analysis, with a chlorinated compound prepared from oil of aniseed, where the amount of chlorine was found to be much larger, sufficiently confirms this. It afforded—

Carbon	51·5
Hydrogen	4·8
Chlorine.....	32·7
Oxygen.....	11·0

But the formula $C^{30} \left.\begin{matrix} H^{14} \\ Cl^{4} \end{matrix}\right\} O^{4}$ requires 49·9 carbon, 3·8 hydrogen, and 38·5 chlorine.—Liebig's *Annalen*, Feb. 1848.

Action of Chlorine upon the Benzoate of Potash. *By* E. St. Evre.

When a slow continuous current of chlorine is passed into a strongly-alkaline solution of benzoate of potash, an abundant disengagement of carbonic acid results after some time, with the formation of chloride of potassium; in this reaction a portion of the carbon of the benzoic acid is oxidized, and there must consequently be formed a substance, the molecule of which is more simple. This view is fully confirmed by analysis. The new body is an acid, which is precipitated in the state of a salt of potash, which after purification yields the acid by decomposition with sulphuric acid. The new acid, after being purified by frequent recrystallization, melts between 176° and 182°, and is volatile. On analysis it furnished numbers leading to the formula $C^{12} H^5 Cl O^4$, which was confirmed by examination of its silver salt. If from this chlorinated product we go back to a compound represented by $C^{12} H^6 O^4$, which may be regarded as the expression of the primitive substance, we arrive at a formula which differs from that of the hydrate of phenyle by containing 2 additional atoms of oxygen. But this is likewise the relation which acids bear to their aldehydes, and the new acid may for the present be called monochlorophenic acid. If we were acquainted with phenylic acid, $C^{12} H^6 O^4$, this should yield phenylene, $C^{10} H^6$, on distillation with caustic alkalies; and the latter should furnish, on treatment with nitric acid, a compound, $C^{10} H^5 NO^4$; from which, lastly, on solution in an alcoholic solution of ammonia and treatment with sulphuretted hydrogen, we ought to obtain nicotine, $C^{10} H^7 N$.

Now this actually occurs quantitatively in the treatment of the above body, but with the qualitative difference that the atom of chlorine, which in comparing the formulæ $C^{12} H^5 ClO^4$ and $C^{12} H^6 O^4$ appears as the substitute for 1 equiv. of hydrogen, likewise passes into all the bodies derived from it. Thus the author obtained,—I. monochlorophenylene, $C^{10} (H^5 Cl^6)$; II. hyponitrate of chlorophenylene, $C^{10} (H^4 ClNO^4)$; and lastly, III. chloronicotine, $C^{10} H^6 ClN$.

Cuminic and margaric acids furnish similar results. By the same treatment to which the benzoic acid was submitted, two new bodies were obtained from suberic acid, one of which is liquid and the other solid.—*Comptes Rendus*, vol. xxv. p. 912.

On the Occurrence of Urea in the Vitreous Humour.
By M. Millon.

The vitreous humour of the eye of the ox leaves on drying 1·63 per cent. residue. According to Berzelius, it contains chloride of sodium, some albumen and organic matters soluble in water. This residue contains, according to Millon, from 20 to 35 per cent. urea. He is of opinion that this fluid consists essentially of chloride of sodium and urea. The vitreous humour of the human eye and that of the dog have a similar composition. Urea and chloride of sodium likewise occur in the aqueous humour.—*Comptes Rendus*, xxvi. p. 121.

Notice respecting the new Alkaloid Quinidine.
By F. L. Winckler.

This alkaloid occurs in one of the new barks most resembling Huamalies. It is accompanied in this bark by quinine; but of the two alkaloids the latter is present in least quantity. It crystallizes from its solution in alcohol in crystals resembling amygdaline, which are somewhat hard like sugar to the touch, and appear under the microscope to be colourless rhombic tablets. It dissolves more readily in alcohol than cinchonine, but less so than quinine; it is very sparingly soluble in water. The sulphate of quinidine can scarcely be distinguished from the sulphate of quinine, and it only differs by its greater looseness from cinchonine precipitated by ammonia from a solution of the sulphate. The compound of chloride of quinidine with chloride of platinum cannot be distinguished externally from the corresponding quinine salt. It leaves 26·4 per cent. platinum.

When sulphate of quinidine occurs in sulphate of quinine, the solution of the mixture is precipitated with carbonate of soda and the alkaloids dissolved in alcohol of 0·863 spec. grav. The quinidine soon crystallizes.—Buch. *Rep.*, xlviii. p. 385.

On the Behaviour of Vegetable Charcoal towards Chlorine, Iodine, Bromine, Chloride of Lime and Hyponitric Acid. By Prof. C. F. Schönbein.

Vegetable charcoal destroys ozone very rapidly. The resemblance which ozone bears to chlorine, iodine and bromine led to the following experiments:—1. When so much chlorine is mixed with atmospheric air that the gaseous mixture appears yellowish, instantly colours iodide of potassium paste blackish-blue, and immediately bleaches indigo paper,—the chlorine instantly disappears on shaking the gas with charcoal powder. 2. When chlorine is passed through a glass tube filled with charcoal powder, the charcoal becomes heated; and only when this has extended throughout the whole length of the charcoal, does the chlorine make its appearance at the other end of the tube. The charcoal thus treated does not evolve the odour of chlorine, and when exposed to the air gives off muriatic acid vapours; when treated with water, it does not part with chlorine, but only with muriatic acid; nor does it disengage chlorine when heated, but it decomposes iodide of potassium, destroys indigo, and turns tincture of guaiacum blue; this property, however, it loses by long exposure to the air. 3. When chlorine water is shaken with charcoal powder, it is quickly deprived of its colour, odour and bleaching power, and the liquid contains muriatic acid. 4. The same is the case with a solution of the hyperchlorite of lime. 5. The brown liquid from peroxide of manganese and muriatic acid is quickly decolorized by being shaken with charcoal powder, and deprived of its odour and bleaching power, that is to say, the chloride of manganese is reduced to protochloride. 6. The most dense atmosphere of bro-

mine vapour is absorbed by charcoal powder even at a temperature of 212°. If charcoal powder and liquid bromine are quickly triturated together, but little bromine is lost; most of it is absorbed by the charcoal, which does not part with any bromine at 212°, but only at a higher temperature. 7. An aqueous solution of bromine is wholly deprived of its bromine by charcoal powder. 8. Vapours of iodine are quickly absorbed by charcoal powder even at 212°; when 1 part of iodine is triturated with 9 parts of charcoal powder, this mixture does not disengage a trace of iodine even at 212°. This combination of iodine and charcoal turns guaiacum tincture blue, just as iodine. Brownish-yellow iodine water can be instantly and entirely decolorized by charcoal powder. 9. Schönbein had previously shown that charcoal powder eliminates hyponitric acid from the first hydrate of nitric acid without any carbonic acid being formed. The author explained this according to his view of the constitution of nitric acid, assuming that the hydrate of nitric acid = $NO^4 HO^2$ is separated into NO^4 and HO^2, when the HO^2 is decomposed without carbonic acid being produced. When a glass tube is filled with a mixture consisting of 9 parts of water and 1 part hyponitric acid, a violent disengagement of nitric oxide results, but no carbonic acid is formed.—Poggendorff's *Annalen*, lxiii. p. 326.

New Method of preparing Chloroform. By Prof. Böttcher.

Equal parts of chloride of lime and acetate of soda are distilled to dryness in an iron retort. But little chloroform is obtained in the first distillation, but a large quantity of dilute acetone, which is mixed with chloride of lime and submitted to a second distillation. But the whole of the acetone is not decomposed in this operation, and it is consequently necessary to mix the product with more chloride of lime, and again distil. The product is rectified over caustic lime. This method is said to effect a great saving.—*Polytech. Notiz-Blatte*, No. 1.

On the Crystalline Form of Metallic Zinc. By J. Nicklès.

The author observes, that the crystalline form of pure zinc has already been described by M. Noeggerath*, who found this metal in prisms with hexagonal bases. Zinc, antimony and arsenic, are then the only crystalline metals, the form of which does not belong to the regular system. The metals of the magnesian series do however crystallize in this system; and if zinc has hitherto formed an exception, it may be hoped that dimorphism will eventually connect this metal with the group of metals to which it belongs by its chemical properties; and the author mentions that he is enabled to state this fact already with respect to some crystals of pure zinc prepared by M. Favre according to the process of M. Jacquelain.

These crystals are very distinct pentagonal dodecahedrons, very similar to the form of iron pyrites and gray cobalt.

* Poggendorff's *Annalen*, vol. xxxix. p. 324.

This example of dimorphism is not unique among metals. Prof. Miller, who has examined the crystalline form of tin, has shown that it crystallizes in the system of the prism with a square base. M. Frankenheim has observed the same metal crystallized in cubes; and very lately Prof. G. Rose* has announced that platina and iridium are isodimorphous. Both crystallize in the rhombohedric and cubic system.

According to these statements, it will not be surprising to observe antimony and arsenic subject to the common law, and belonging to the regular system, which appears really to be that of all the metals.—*Ann. de Chem. et de Phys.*, Jan. 1848.

ANALYTICAL CHEMISTRY.

On a new Method of estimating Arsenic, Antimony and Tin. *By* Prof. H. Rose†.

Chloride of ammonium can be usefully employed in analytical investigations, from its property of decomposing several oxides at a high temperature and forming with the metals highly volatile chlorides. The experiments frequently give far more accurate results, in the shortest time and with the least trouble, than have hitherto been obtained by the usual methods of analysis.

It is well known what difficulties accompany the separation of the acids of arsenic and of antimony, as likewise that of the peroxide of tin, from bases. In general these metallic acids are separated from the solutions of most of their salts in hydrochloric acid, or to which hydrochloric acid has been added, by sulphuretted hydrogen, as sulphurets, and the base in the filtered liquid determined in the state of chloride. If the latter happens to be one which is easily decomposed at an elevated temperature, and not volatile or only so at a very high temperature, the liquid, which is frequently very considerable in quantity, has to be evaporated to dryness, and the residue ignited more or less strongly. Every one accustomed to analytical investigations must be sufficiently well acquainted with the inconveniences which accompany the evaporation of large quantities of liquids containing small amounts of alkaline salts, which have to be determined quantitatively.

The difficulties attending such an investigation become greater when the salt of the metallic acid is not at all, or very sparingly, soluble in water and in hydrochloric acid, or one which is easily decomposed. Now this is frequently the case with a salt of this class when it has been heated to redness, which is requisite in determining the amount of water directly.

All these difficulties may in many cases be avoided by the use of chloride of ammonium. Suppose we have a salt of one of these metallic acids with an alkaline base to examine, it is only requisite to mix it, after having ignited and weighed it in the finely-pulverized state, with from five to eight times the quantity of pure powdered

* Poggendorff's *Annalen*, vol. lv. p. 329. † Communicated by the Author.

chloride of ammonium, and to heat the mixture in a small porcelain crucible which may be covered with a concave platinum lid, over an Argand lamp until the whole of the chloride of ammonium is volatilized. The alkali is left behind in the state of chloride, the quantity of which may be very accurately determined. So long as chloride of ammonium is volatilized, the temperature is so low that none of the alkaline chloride can escape. As soon as the ammoniacal salt is driven off, the temperature is moderated, so that the residue in the porcelain crucible does not fuse. After weighing, it is mixed with a fresh quantity of chloride of ammonium and again heated, in order to see whether the weight of the residue remains constant or is diminished, in which latter case the treatment with chloride of ammonium must be repeated. Sometimes, owing to the access of air, the platinum lid is coated with a film of the metallic acid, especially with peroxide of tin when stannates are examined. In this case, the lid, in the subsequent ignition, is covered with a little of the ammoniacal salt.

I will here describe some experiments which have been made by M. Weber:—0·609 grm. of ignited *arseniate of soda*, $2NaO + AsO^5$, afforded, after being once treated with five times the amount of chloride of ammonium, 0·455 grm. chloride of sodium. The weight remained the same after repeating the treatment with chloride of ammonium. The quantity of chloride of sodium corresponds to 35·46 per cent. soda in the salt; the theoretical quantity is 35·18.

1·048 grm. *antimoniate of soda* ($NaO\ SbO^5 + 7HO$), the amount of soda in which, according to Fremy's analysis, is 11·9 per cent., afforded, after five ignitions with chloride of ammonium, a constant weight of 0·429 grm. chloride of sodium, which corresponds to 12·58 per cent. of soda; the salt had been dried for a length of time at 212°, and it is possible that it had lost some of its water of crystallization.

Stannate of Potash.—This salt had been precipitated by alcohol from the solution of the peroxide of tin in hydrate of potash, washed with alcohol, then dissolved in water and evaporated. It formed, after drying under the air-pump over sulphuric acid, a gummy mass, which again easily dissolved in water; it contained the *b*-modification of the oxide of tin. According to an examination after the usual method, the salt dried at 212° consisted, in 100 parts, of—

87·34 peroxide of tin.....	18·67 oxygen.	
8·02 potash	1·35	...
4·64 water	4·11	...

According to this the composition of the salt is $KO + 7SnO^2 + 3HO$. The acid metastannate of potash is, according to Fremy, $KO + 6SnO^2 + 5HO$. It is possible therefore that the salt prepared by me contained a quantity of a still more acid salt mixed with it.

Of the salt used for the above analysis, 1·013 grm. was mixed with 5 times the amount of chloride of ammonium and heated to redness; this was repeated twice with smaller quantities of chloride of ammonium, when the weight of the residue no longer varied; 0·131 grm. chloride of potassium was obtained, corresponding to 8·09 per cent. of potash. All the chlorides obtained dissolved en-

tirely in water, and when tested did not exhibit the least trace of the metallic acids. The use, however, of chloride of ammonium in analytical chemistry is not restricted to the compounds above mentioned; it is capable of considerable extension, as I intend to point out in a subsequent paper.

PATENT.

Patent granted to Arthur Harry Johnson, London, *for Improvements in refining Silver Lead.*

This invention consists in a method of restoring and rendering again available for use the phosphate of lime or bone-ash, whereof the cupel or test used by refiners of silver lead is composed, and which, in the process of refining, becomes saturated with lead and a portion of silver.

The ordinary mode of extracting the lead and silver is by returning the used cupel to the furnace; by which means the whole of the saturated bone-ash is destroyed, while portions of the lead and silver combining with the phosphoric acid of the bone, pass off and are lost; but, as the patentee states, when this improved method is adopted, no waste of bone-ash, lead or silver is occasioned. The peculiar feature of novelty of the invention consists in the use of a solvent of the oxide of lead, and the patentee prefers to conduct the process in the following manner:—The used cupel is reduced to a fine powder, and a sufficient quantity of pyroligneous or acetic acid (varying from 1·030 to 1·048 spec. grav. according to the per-centage of lead contained in the cupel), to produce a mixture of a thin consistence, is added; this mixture is stirred occasionally during a period of two days (by which time the bulk of the lead will be dissolved); it is next put into cloth or flannel filters, or other suitable percolators, in order that the lead solution may drain off; and then the remaining soluble salt of lead is removed by washing with water and by the application of pressure, previous to drying the bone-ash.

The silver and a small quantity of lead still remain in the bone-ash after the above operation, although there is not sufficient lead to materially interfere with the absorbent powers of the bone-ash, or to prevent it from being again used, provided it has been properly freed from the lead solution; but if it should be desired to extract the lead more perfectly, the bone-ash, after being removed from the filters, and before being washed and pressed, is to be subjected to the action of a second portion of acid, stirring the mixture thoroughly.

To bring the lead contained in the above-mentioned solution into a marketable form, the solution may be evaporated to produce sugar of lead; or, by means of the reagents commonly used, the carbonate, sulphate, sulphuret, or other compound of lead, may be obtained.

Instead of pyroligneous acid, the patentee sometimes employs a solution of caustic potash or soda, containing about 20 per cent. of the pure alkali; but he has not found it to answer so well as the acid.—Sealed Sept. 23, 1847.

THE CHEMICAL GAZETTE.

No. CXXXIII.—May 1, 1848.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the gradual Decomposition of the Neutral Acetate of Lead by Caustic Potash. *By* Prof. TADDEI*.

WHEN to a solution of neutral acetate of lead having a density of 1·25 to 1·30, a solution of caustic potash of a density 1·06 is added drop by drop, a momentary turbidity is produced at the points of contact of the two liquids; but on agitation the solution assumes its primitive limpidity, and becomes capable of taking up a much greater quantity of potash without becoming turbid or giving rise to a precipitate, provided the alkali is added in successive small quantities and the solution is maintained at the temperature of ebullition. If a slight turbidity is produced on mixing the two liquids, the limpidity is soon restored, and the solution exhibits an increased capacity for a further quantity on continuing the ebullition for some time, and avoiding as much as possible the influence of the carbonic acid of the atmosphere; for which reason it is advisable to conduct the operation in close vessels, in a retort, for example, furnished with a recipient, and having a tube fitted into the tubulure of the retort descending to the bottom of the boiling solution.

On continuing the addition of the caustic alkali in small quantities, while the liquid is in a state of ebullition, a point is arrived at when the solution suddenly becomes a solid magma of snowy whiteness similar to the coagulum produced in milk by the action of rennet, and which is not entirely owing to the evaporation of the water.

This mass having the appearance of a caseous coagulum, is formed by a basic double salt, which has not hitherto been examined; it dissolves at the temperature of ebullition in a moderate quantity of water, in which, unless the carbonic acid gas has been expelled from the water by boiling, a slight milkiness is produced, without losing the property of taking up an additional quantity of alkali.

The solution of the basic salt, on exposure to the air, becomes covered with a pellicle like the other basic salts of lead; a considerable precipitate is produced by a current of carbonic acid, or when treated with neutral sulphates or carbonates, or with soluble chlorides. When the solution is evaporated at a gentle heat until considerably concentrated, it becomes covered with a pellicle or

* We are indebted for this communication from the Italian to the kindness our friend T. H. Henry, F.R.S.

crust of a pearl-white colour, slightly translucent, and concretes to a mass composed of scales or laminæ similar to that produced on the cooling of a hot saturated solution of cholesterine, and is composed of a confused mass of extremely delicate filiform crystals crossing one another in every direction.

The crystalline mass gives off water at 212° F., losing the appearance of mother-of-pearl and the original form of most of the crystals, and becomes pasty, resembling sulphate of quinine when moistened with a small quantity of water. It supports a temperature of 662° F. without fusion, decrepitates, and loses about 12 per cent. in addition to what it previously lost at 212° F.; which amount, however, is far from representing the quantity of water existing in the salt, as it combines with more or less carbonic acid during the operation. The dry mass becomes amorphous, but remains white, and attracts moisture from the atmosphere. A little below a red heat it fuses and decomposes, giving off carbonic acid gas, acetone and empyreumatic matters, which burn with flame, leaving a black carbonaceous residue, which deliquesces in the air. This residue consists of carbonate of potash, oxide of lead and metallic lead, which may easily be separated by treatment with dilute acetic acid. On heating the carbonaceous residue to redness in an open vessel, the greater part of the lead is oxidized, forming a semi-fused mass of a beautiful yellow colour, soluble in acids with effervescence, owing to the carbonate of potash it contains.

Into the solution of the above-mentioned saline mass a current of sulphuretted hydrogen was passed, and the sulphuret of lead separated by filtration; the liquor no longer exhibited an alkaline reaction. The sulphuret was repeatedly washed with hot water until the washings left nothing on evaporation; and these being added to the previous solution, the whole was concentrated. Hydrochloric acid was added in excess to decompose the acetate of potash, the whole evaporated to dryness in a platinum crucible, and the heat finally raised to dull redness, in order to decompose a portion of the acetate which had escaped the action of the hydrochloric acid; the residue was again treated with hydrochloric acid and heated to expel the excess, the chloride of potassium dissolved in water and precipitated by nitrate of silver, the chloride of silver and the sulphuret being well-dried, the weight of the oxide of lead was calculated from one, and that of the potash from the other, the two bases of the double salt under consideration. I found for 52·58 grs. of oxide of lead 14·78 grs. of potash. The quantity of acetic acid with which these two bases were combined was the same as would be required to form a neutral salt with the oxide of lead, that is 64·31 for every equivalent of oxide of lead = 139·45; the 52·58 grs. would have required therefore 24·56 grs. of acetic acid. The salt therefore consists of—

			Experiment.	Calculation.
Potash	14·78	or per cent.	16·08	16·178
Oxide of lead.....	52·58	...	57·20	57·364
Acetic acid	24·56	...	26·72	26·458
	91·92		100·00	100·000

This will afford—

4 atoms of potash	58·99	× 4	=	235·96
+6 atoms of oxide of lead	139·44	× 6	=	836·64
+6 atoms of acetic acid	64·31	× 6	=	385·86
				=1458·46

The empirical formula will be $4KO + 6PbO\,\overline{A}$, in which, if the acetic acid be divided between the two bases in such a manner that the potash is neutralized by it, 4 atoms of oxide of lead will remain uncombined; thus two salts will result, one neutral and the other tribasic, in a state of chemical combination, as will be seen from the following formula:—

$$4(KO, \overline{A}) + 2(Pb^3 O^3, \overline{A}),$$

or 4 equivs. of neutral acetate of potash $4(KO, \overline{A})$	= 493·20
with 2 equivs. of tribasic acetate of lead $2(Pb^3 O^3, \overline{A})$	= 965·26
	1458·46

Decomposing Action of Carbonic Acid.

In estimating either of the bases of this compound, however, it should be remembered, that during the various manipulations, in the contact of air or water never altogether free from carbonic acid, the conversion of a portion of the tribasic acetate of lead into carbonate is unavoidable; whence a quantity of oxide of lead separates from the solution, corresponding not only to the carbonate produced, but also to the sexbasic acetate of lead simultaneously formed, and which being equally insoluble, ceases to form part of the double salt under consideration. Neither does the action produced by the presence of the carbonic acid stop here, for the formation of the carbonate and sexbasic acetate is accompanied with the transformation of another portion of the tribasic acetate of lead into neutral acetate.

In fact, if the double salt in question be represented as consisting of 8 equivs. of acetate of potash and 4 equivs. of tribasic acetate of lead, and it be treated with carbonic acid gas until the decomposing action ceases, an absorption of 3 equivs. of this gas will have taken place, and the results of the decomposition will be such as are represented in the following equation:—

$$8(KO,\overline{A}) + 4(Pb^3O^3,\overline{A}) + 3CO^2 = \begin{cases} 8(KO,\overline{A}) + 3(PbO,\overline{A}) \text{ soluble.} \\ +3(PbO, CO^2) + Pb^6O^6, \overline{A} \text{ insoluble.} \end{cases}$$

Whence it is evident that, a fresh portion of neutral acetate of lead being formed in the double salt, the compound will become capable of combining with a fresh quantity of potash without giving rise to a precipitate, and precisely as much as may be required to transform the neutral acetate of lead into the tribasic—

$$8(KO, \overline{A}) + 3(PbO, \overline{A}) + 2KO, = 10(KO, \overline{A}) + Pb^3 O^3, \overline{A}.$$

It is therefore evident that the action of carbonic acid on the double salt in question gives rise to a triple change in the relation of the bases contained in it, both by separating a portion of the oxide of

lead in an insoluble form (carbonate and sexbasic acetate), and by reproducing the neutral acetate in the portion remaining in solution, the capacity of saturation for the alkali is increased.

It is possible to render almost inappreciable the action of the carbonic acid, by operating in the manner above described, making use of potash recently rendered caustic, and of distilled water previously boiled, and moreover by expelling the air contained in the apparatus by boiling the solution of acetate of lead previous to adding the caustic potash.

Series of Decompositions experienced by the Neutral Acetate of Lead under the gradual (interrupted) action of Caustic Potash.

Assuming that the double salt under examination is a compound represented by the formula $4(KO, \bar{A}) + 2(Pb^3 O^3, \bar{A})$, it appears to me reasonable to admit, that in producing by means of caustic potash the gradual decomposition of neutral acetate of lead, it will pass through the following series of metamorphoses previous to arriving at the composition above mentioned.

If we take, for example, 6 atoms of the neutral salt, the decompositions successively taking place should occur as expressed in the following equations:—

Neutral acetate of potash. Neutral acetate of lead. Sesquibasic acetate of lead.

I. $6(PbO, \bar{A}) + KO = KO\bar{A} + 3(PbO, \bar{A}) + Pb^3 O^3 \bar{A}^2$.

Neutral acetate of potash. Sesquibasic acetate of lead.

II. $KO, \bar{A} + 3(PbO, \bar{A}) + Pb^3 O^3 \bar{A}^2 + KO = 2(KO, \bar{A}) + 2(Pb^3 O^3 A^2)$.

Neutral acetate of potash. Sesquibasic acetate of lead. Tribasic acetate of lead.

III. $2(KO, \bar{A}) + 2(Pb^3 O^3 \bar{A}^2) + KO = 3(KO, \bar{A}) + Pb^3 O^3 \bar{A}^2 + Pb^3 O^3 \bar{A}$.

Neutral acetate of potash. Tribasic acetate of lead.

IV. $3(KO, \bar{A}) + Pb^3 O^3, \bar{A}^2 + Pb^3 O^3 \bar{A} + KO = 4(KO, \bar{A}) + 2(Pb^3 O^3, \bar{A})$.

From these formulæ it is clearly apparent that, on the abstraction of every atom of acetic acid from the lead salt by the addition of an atom of potash, a corresponding portion of the lead salt passes to the basic state. And as the quantity of the new salt formed (neutral acetate of potash) increases by single equivalents from 1 to 4, so in the acetate of lead the acetic acid decreases in the same ratio, or by 1 equiv. at a time, diminishing from 6 to 2; by which the neutral acetate of lead, during the gradual decomposition it undergoes under the action of the caustic potash, is transformed first into sesquibasic acetate $2(Pb^3 O^3, \bar{A}^2)$, afterwards into tribasic acetate $2(Pb^3 O^3, \bar{A})$; transformations only partial at the commencement, but complete in the end, and taking place in constant and determinate quantities.

Ulterior and final Transformation of the Tribasic Acetate of Lead contained in the Double Salt.

This is not the point to which the decomposition of the lead salt is limited however by the action of the caustic potash; by continuing the addition it passes to a lower basic state (sexbasic), and finally is deprived entirely of its acetic acid.

The decomposition it undergoes is moreover influenced not only by the relative proportions of the alkali and the salt operated on, but also by the greater or less quantity of liquid in which they are dissolved, and lastly by the temperature at which the decomposition is effected.

When the double salt $4(PbO, A)+2(Pb^3 O^3, A)$, moderately concentrated, is decomposed by caustic potash in quantity sufficient to neutralize the whole of the acetic acid combined with the tribasic salt of lead contained in it, the oxide of this metal is totally precipitated in the form of a white pulverulent hydrate; while, on the contrary, when the alkali is employed in excess, the precipitate disappears, or if a considerable excess be added at once, no precipitate or cloudiness is produced, the oxide of lead being dissolved in the excess of alkali as soon as separated from the acetic acid.

Again, if the double salt is dissolved in 20 to 30 times its weight of water, the caustic potash causes no precipitate and scarcely any cloudiness whatever, even when it is added drop by drop; the liquid becomes much more clear by boiling in close vessels; and this because the oxide of lead separated from the acetic acid is redissolved by solution of the acetate of potash when the necessary amount of water is present. On the other hand, if the decomposition of the double salt is effected in a concentrated solution, the caustic potash being added during ebullition, there is instantaneously produced an abundant precipitate of a deep yellow colour, composed of minute scales or brilliant laminæ with a metallic lustre, very similar to *aurum musivum*. These laminæ subside rapidly, and on being separated by decantation and well washed, increase in brilliancy, resembling litharge obtained in the dry way by calcination, except that they are lighter, more easily soluble in acids and alkalies, and more prone to absorb carbonic acid from the atmosphere when moistened by water, or better by an alkaline solution.

To the oxide of lead obtained in this form, and which is rendered anhydrous by the heat of ebullition, the name of *litharge by the moist way* appears appropriate. Although it is much more readily attacked and dissolved by acetic and nitric acids than the common litharge prepared by the dry method, still it does not redissolve in the caustic potash employed in its preparation unless a very considerable excess is used; when, for instance, the process was reversed, and the solution of the double salt was added drop by drop to the caustic potash, in which case the oxide of lead could neither be precipitated nor remain dehydrated.

This litharge by the moist way will not be without its advantage in chemical operations, whether, as compared with that prepared by calcination, its purity and freedom from copper and other metals, be

taken into consideration, or on account of its being more readily attacked by acids, or susceptible of combination with other substances, it will be employed in preference for analytical operations.—*Raccolta Fisico-Chimica Italiana*, vol. ii. p. 562–570.

On the various Compounds of Platinum derived from Magnus's *Green Salt.* *By* M. Raewsky.

The ammoniacal protochloride of platinum, the existence and singular properties of which were pointed out by M. Magnus, has become for several years past the starting-point for several highly important investigations. This compound, which is produced directly by combining ammonia with the protochloride of platinum, is generally known by the name of Magnus's green salt. It is formed of equivalent proportions of protochloride of platinum and ammonia, $PtCl, H^3 N$. Caustic alkalies, concentrated hydrochloric and sulphuric acids have no action upon this salt in the cold; it is only after long boiling that the ammonia is expelled or removed by these powerful reagents, and in this respect the ammoniacal protochloride of platinum behaves like a true amide.

On examining the action of nitric acid upon Magnus's green salt, M. Gros discovered, some years ago, a new series of salts, the complex composition of which is, in the present state of the science, difficult to define by the present nomenclature; and undoubtedly, on account of this difficulty, they have been called after the name of their discoverer. Still more recently, M. Reiset, in a memoir remarkable for the new and important facts it contained, described two other series of salts of platinum, equally derived from the ammoniacal protochloride. The author has also submitted Magnus's green salt to further experiment, and has found that this compound is capable of yielding two new series of salts, into the composition of which platinum and the elements of ammonia enter.

When nitric acid acts upon certain samples of Magnus's green salt, it sometimes leaves a residue, which had been looked upon as metallic platinum, the formation of which could not be explained. The author shows clearly that this deposit is not formed with a perfectly pure substance, and that its origin must be sought for in the green salt itself when it has begun to undergo decomposition from being dried at too high a temperature. The ammoniacal protochloride of platinum in yellow crystals, isomeric with the green salt, and which is far more easy to obtain pure, never leaves a residue insoluble in nitric acid.

Gros's platinum salts are formed alone, or accompanied with two other series of salts, according as the green salt is treated with more or less considerable proportions of nitric acid. The following is a simple and ready method of preparing Gros's salts:—It suffices to boil a small quantity of dilute nitric acid with the ammoniacal protochloride of platinum. A considerable quantity of a nitrate is obtained, the composition of which, according to M. Raewsky, agrees perfectly with the formula $PtClO, N^2 H^6, NO^5$, assigned to it by

M. Gros. An excess of concentrated nitric acid no longer gives rise to this nitrate, but produces simultaneously two new compounds, which both contain a base capable of being combined with several acids by double decomposition. Regarding the salts of M. Raewsky in the ordinary manner, and admitting that they contain the acids employed to prepare them, analysis assigns to these two nitrates the following composition :—

1. Salt sparingly soluble in nitric acid, $P^2\,ClO^5$, $N^4\,H^{12}$, $2NO^5$.

2. Salt very soluble in nitric acid, and crystallizing with difficulty on concentrating the mother-ley of the first nitrate, $Pt^2\,Cl^2\,O^4$, $N^4\,H^{12}$, $2NO^5$.

The formation of the two preceding salts takes place according to the following equation :—

$$8PtClNH^3 + 24NO^5, HO = Pt^2\,ClO^5, N^4\,H^{12}, 2NO^5 + Pt^2\,Cl^2\,O^4, N^4\,H^{12}, 2NO^5 + 4PtO^2, (NO^5)^2 + 19HO + 5HCl + 12NO^4.$$

The salt 1. is very readily obtained pure; it crystallizes in small brilliant needles, deflagrates when heated, disengaging water and chloride of ammonium, and leaving a residue of metallic platinum. Caustic alkalies do not act upon it in the cold, but on the application of heat they expel ammonia. It presents the characteristic properties of the nitrates. Nearly all the salts of this base are less soluble than the corresponding nitrates, and were obtained by double decomposition. Thus the phosphate is obtained by adding phosphate of soda to a hot and concentrated solution of the nitrate; nitrate of soda is formed, and the phosphate of M. Raewsky's base being sparingly soluble, is deposited. The oxalate, the carbonate, the neutral chromate and the bichromate were prepared without difficulty; but the sulphate and the acetate could not be obtained, owing undoubtedly to their greater solubility.

The nitrate, $Pt^2\,ClO^5$, $N^4\,H^{12}$, $2NO^5$, exhibits the curious property of being readily decomposed by hydrochloric acid, which converts it into a salt of the second series with the formula $Pt^2\,Cl^2\,O^2$, $N^4\,H^{12}$, Cl^2, which differs by its great solubility from the compounds belonging to the first class. In the course of his investigation the author observed that the binammoniacal protochloride of platinum of M. Reiset could absorb directly 1 equiv. of chlorine or 1 equiv. of bromine, and that these combinations were effected without giving rise to any phænomenon of substitution, the whole of the hydrogen remaining in the new compound. The action of chlorine upon the binammoniacal chloride of platinum yields two compounds, one of which is M. Gros's hydrochlorate, while the other represents the same compound united to 1 equiv. water. In fact, we may admit in the nitrate of M. Gros ($PtClO$, $H^6\,N^2$, NO^5) the existence of the base $PtClO$, $N^2\,H^6$; and this, on treatment with hydrochloric acid, furnishes a chloride according to the following reaction :—

$$PtClO, H^6\,N^2 + HCl = HO + PtCl, H^6\,N^2, Cl.$$

Comptes Rendus, xxv. p. 794.

On the Absorption of Carbonic Acid by Sulphuric Acid.
By H. M. Noad, Esq.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—In the 'Chemical Gazette' for March 15th of the present year I read the somewhat startling announcement, on the authority of Prof. W. B. and R. D. Rogers, "that sulphuric acid at the temperature of 60° F. absorbs carbonic acid gas in the large proportion of 94 per cent., and that Nordhausen acid absorbs 125 per cent." It is further stated, that this fact must lead to serious errors in the analyses of carbonates by the process invented by Drs. Fresenius and Will. Being myself in the frequent habit of employing the simple and elegant method of the German chemists in alkalimetrical experiments, and having invariably obtained perfectly satisfactory results, I needed no further experiments to convince myself that the objections raised by Prof. Rogers are without foundation. As, however, no refutation of the statement of the American chemist has (to my knowledge) been hitherto published, I venture to send you the results of a few experiments on the subject which I have this day made, and for which you may perhaps find room in your next Journal.

Carbonate of Soda,
prepared by igniting pure bicarbonate.

Ex. 1.—70 grs. lost 28·99 grs. of carbonic acid = 41·41 per cent.
Ex. 2.—64·6 grs. lost 26·8 grs. of carbonic acid = 41·48 per cent.
Theory requires 41·54 per cent.

1 equiv. of NaO.....	30·97	58·46
1 equiv. of CO^2	22·00	41·54
1 equiv. of NaO, CO^2	52·97	100·00

Carbonate of Potash,
prepared by igniting the pure bicarbonate.

Ex. 1.—79·24 grs. lost 25·2 grs. of carbonic acid = 31·81 per cent.
Ex. 2.—90·55 grs. lost 28·84 grs. of carbonic acid = 31·84 per cent.
Theory requires 31·88 per cent.

1 equiv. of KO	47	68·12
1 equiv. of CO^2	22	31·88
1 equiv. of KO, CO^2	69	100·00

Carbonate of Strontia,
prepared by precipitating solution of chloride of strontium by an alkaline carbonate.

78·84 grs. lost 22·75 grs. of carbonic acid = 29·75 per cent.
Theory requires 29·8 per cent.

1 equiv. of SrO	51·84	70·20
1 equiv. of CO^2	22·00	29·80
1 equiv. of SrO, CO^2.....	73·84	100·00

These experiments are quite satisfactory as to the degree of confidence to be reposed in the German method; indeed, any one who has either gone through the manipulations, or read the directions given by the authors in their work, will see at once that, even supposing sulphuric acid to have the property ascribed to it by Prof. Rogers, of absorbing so large an amount of carbonic acid, it cannot in the least interfere with the correctness of the method, inasmuch as whatever carbonic acid gas may have been absorbed by the sulphuric acid during the decomposition of the carbonate, it must be all removed by the subsequent operation of drawing a stream of atmospheric air through the apparatus.

In order, however, to see whether the sulphuric acid remaining in the small bottle really did absorb a large amount of carbonic acid, I made an experiment in which I weighed the apparatus both previous to and after sucking air through the bottles. The particulars are as follows:—

43·67 grs. of carbonate of soda lost 17·75 grs. of carbonic acid, atmospheric air *not* having been drawn through the bottles = 40·64 per cent., a deficiency amounting to 0·77 per cent.

The wax stopper was then removed from the vertical tube in the larger bottle, and air drawn through the liquids for some time; the loss now amounted to 18·15 grs., giving 41·55 per cent. for the proportion of carbonic acid.

The difference in the two weighings is less than half a grain; and when it is considered that the space above the liquid in both bottles was filled with carbonic acid, which was removed and replaced by atmospheric air in the process of sucking, it is at once evident that the quantity of carbonic acid absorbed by the sulphuric acid must be very trifling.

I am, Sir,

1 New Millman Street, Russell Square,
26th April, 1848.

Your obedient Servant,
HENRY M. NOAD.

On the Reaction of Solid Carbonic Acid with Alkaline and other Bases. *By* WM. F. CHANNING, M.D.

1. The production of heat by the reaction of solid carbonic acid with a caustic alkali was noticed by me in this Journal for January 1844*. A more precise series of observations on the same reaction, extended to a greater number of bases, will be found to afford some additional facts in the history of the acid, and to illustrate a most striking instance of the evolution of heat by chemical union. The details of manipulation will be preserved in the following experiments, chiefly to indicate the best mode of exhibiting the phænomena described.

2. Solid carbonic acid was placed in contact successively with different bases, presented to it for the most part in the dry state. The intensity of the reaction and the amount of heat produced were generally estimated by the effects of ignition and fusion obtained. The heat being local, and one of the substances present being in a

* See Chem. Gaz., vol. ii. p. 140.

state of intense refrigeration, it was found that no accurate measurement could be made by employing a thermometer either in contact or subjected to radiation.

3. A small fragment of solid carbonic acid was comminuted as much as possible, and placed on cotton-wool. A little pure pulverized hydrate of potash was poured upon it. A piece of gun-cotton was laid over these, the whole covered with cotton-wool, and compressed by a spatula. In a few seconds the gun-cotton exploded. Gun-cotton compressed with either carbonic acid or hydrate of potash separately showed no disposition to ignite.

4. Pure hydrate of soda was substituted for hydrate of potash with a similar result, acting apparently with equal intensity. The pure hydrates of soda and potash, evaporated in silver vessels, contain frequently some additional water to the one atom belonging to the hydrate, which interferes with the above reaction. Thus if the cylinders of common hydrate of potash, which is evaporated at a higher heat in iron vessels, are employed, the reaction is more intense and the result more immediate. That this is not occasioned by the presence of carbonate of potash, existing as an impurity in the hydrate, is shown by subjecting protocarbonate of potash itself to reaction with the carbonic acid. In this case no sensible heat is evolved. The energetic reaction of solid carbonic acid with the alkalies seems to terminate with the formation of protocarbonate. Pure potash was also mixed with quicklime, and then treated with the carbonic acid, but without any increase of action.

5. The alkaline earths were heated to redness in a platina capsule before each experiment, and employed as soon as cooled. Anhydrous lime exposed to solid carbonic acid gave no indications of heat or reaction. The lime was then carefully hydrated by adding drops of water. Subjected to solid carbonic acid, reaction now took place, but the heat was sensibly less than when hydrate of potash was employed. Gun-cotton remained unignited. A little of the hydrate of lime was placed upon tinfoil. A piece of solid carbonic acid, flattened by the spatula, was placed upon the hydrate of lime and covered with an additional quantity of the same. The tinfoil was then wrapped up and compressed. The heat evolved was too great to be borne by the hand, and caused a fragment of phosphorus placed upon the foil to ignite.

6. Anhydrous baryta, strontia and magnesia gave no reaction with the carbonic acid. Their hydrates all produced heat, slightly less perhaps than that evolved by hydrate of lime.

7. It might have been anticipated that the reaction of the alkaline earths with solid carbonic acid would be more energetic than that of the alkalies from their habitudes in solution. But the decisive fact of the superior affinity of the alkalies for carbonic acid in the dry state would lead us to infer that the result in solution is due to the "influence of insolubility" in the precipitated carbonates of the alkaline earths.

8. It seemed desirable to extend the inference that carbonic acid does not combine directly with an anhydrous base. Potassium was

therefore cut into thin layers, and allowed to oxidate in the air. From the great disposition however of solid carbonic acid to condense moisture on itself, and the liability of the mingled potash and potassium to ignite spontaneously or by slight causes, no accurate result could be obtained. There was no evidence of the production of heat by any reaction with the carbonic acid.

9. The anhydrous protoxides of lead, zinc and copper were subjected to solid carbonic acid placed upon cotton. No elevation of temperature could be detected. The hydrates of these oxides, when wrapped in cotton with carbonic acid and compressed by the fingers, gave a doubtful result to the sensation, the temperature being very slightly elevated, if at all.

10. Solid carbonic acid wrapped in gun-cotton was exposed in the open end of a glass tube to dry ammoniacal gas generated at the closed end, and desiccated by passing through a portion of quicklime in the centre of the tube. No striking result was produced, but a sensible heat was obtained, especially at the close of the experiment, when a portion of moisture probably came over with the ammonia. In place of the solid carbonic acid employed, a piece of carbonate of ammonia was found occupying its place in the cotton after the experiment. Gun-cotton, placed alone in the tube, gave no such reaction. The gun-cotton which had been exposed to the gaseous ammonia, it may be remarked, was observed to burn more slowly and with a red flame.

11. Solid carbonic acid was compressed in contact with hydrated acetate of lead, a salt readily attacked by carbonic acid, but no sensible heat was evolved.

12. To obtain some indication of the amount of heat which could be produced by this reaction, common hydrate of potash was pulverized and spread upon tinfoil, a flattened piece of solid carbonic acid placed upon it, and covered again with hydrate of potash. The whole being compressed, gave a heat estimated to be near the melting-point of tin, though actual fusion could not be effected by any arrangement. A splinter of pine brought in contact with the foil was slightly discoloured, and gave the characteristic smell of charred wood. The temperature may therefore be safely estimated at between 350° and 400° F. By substituting a slip of platina foil above and below the reagents in place of the tinfoil, æther, alcohol and water dropped upon it, were successively vaporized. Phosphorus was instantly inflamed on touching the foil. A piece of fusible metal placed upon the foil was melted.

13. Hydrate of potash and solid carbonic acid were ground together in a small mortar. Sufficient heat was produced to explode gun-cotton, but the experiment is an undesirable one for repetition. The experiment with gun-cotton in § 3 may be diversified by placing a portion of cotton wet with alcohol near but not in contact with the gun-cotton. The alcohol is then ignited by the explosion of the latter.

14. The reaction of solid carbonic acid with liquids and solutions is referable to some extent to the same principle as its reaction with

bases in the dry state. When immersed in water, it combines with the latter, and at the same time the evolution of gas is so rapid as to prevent the solid from touching the liquid. Owing to these causes the temperature of the water falls only a few degrees, instead of the anticipated result of immediate congelation, and the thermometer held in the gas escaping from the surface indicates a temperature slightly above that of the surrounding air, this heat being the heat of combination, evolved at the point of union of the carbonic acid and the water, acting as a base. With a solution of potash the reaction is very much the same, the only observable point being the great quantity of gas which escapes absorption.

15. When solid carbonic acid is treated with æther or alcohol, it assumes a semi-fluid state, and no chemical combination probably taking place, and the vaporization of the acid being augmented, these mixtures become of the most frigorific character, and are commonly used for this purpose. When however hydrate of potash is added to these in a mortar, the mixture with æther rises to a temperature probably above 40° F., and that with alcohol still higher, with occasional violent ebullition.

16. Taking the temperature of solid carbonic acid at −148° F., and the greatest heat obtained by its reaction with the hydrated alkalies at from 350° to 400° F., there is an elevation of temperature produced in this case of more than 500° F. As this scale goes far below as well as above the natural temperature, it affords an opportunity of exhibiting the effects of intense cold and intense heat side by side and proceeding from the same substance. These experiments have therefore an illustrative value in connexion with heat and chemical affinity, as well as with the properties of carbonic acid in the solid state.—Silliman's *Journal*, March 1848.

On the Decomposing Power of Water at high Temperatures. *By* Richard Tilghman, A.M.

This paper shows that the vapour of water, passed over various substances at a high heat, has power to decompose them with the evolution of their constituents. The anhydrous chloride of calcium and the chlorides of strontium and barium were rapidly decomposed by passing over them, at a high red heat, a current of steam; hydrochloric acid was copiously evolved, while the bases were left pure and the lime anhydrous. The same decomposition was also observed in case of various sulphates (oxysalts as they are usually called), *e. g.* sulphates of magnesia, lime, strontia and baryta. The heat required for their decomposition is higher as the amount of their basic power is greater. The sulphate of magnesia gives off its acid in a current of steam at a low red heat, while the sulphate of lime requires a high red heat, and of baryta a low white heat. At a full white heat the subphosphate of lime was decomposed, with slow evolution of its phosphoric acid. Lime, magnesia, and particularly alumina, were found to aid materially by their presence in the decomposition of the sulphates and chlorides of potash and soda, which

alone suffer only an imperfect decomposition by the agency of hot aqueous vapour, because of the volatility of the hydrates of these alkalies at a high heat.

As potash alum is completely decomposed by steam at a high temperature, analogy of constitution led our author to the belief that felspar (which has the same constitution as potash alum, changing silicic acid for sulphuric) would also suffer the same change, and experiment confirmed the conjecture. Partial fusion of the fragments of felspar was the only visible change now produced; these fragments however being pulverized and boiled in water, the concentrated solution was strongly alkaline, and proved to contain aluminate of potash. Dilute sulphuric acid also produced a small portion of alum from the powder which had been exhausted with water. —*Trans. Amer. Phil. Soc.*, vol. x. part 2.

On the Pyrophosphates. By Dr. A. Schwarzenberg.

As the preparation of large quantities of pyrophosphoric acid by decomposition of the pyrophosphate of lead with sulphuretted hydrogen is very difficult, the author attempted to separate the acid from the lead salt by means of sulphuric acid. The excess of sulphuric acid was removed by the addition of some barytic water; but if more of the latter was added than was exactly requisite to separate the sulphuric acid, the pyrophosphate of baryta formed remained dissolved in the pyrophosphoric acid; while if a trace of sulphuric acid remained unseparated, the pyrophosphoric acid soon changed into the ordinary phosphoric acid, and it was therefore necessary to adhere to the usual mode of preparation.

Pyrophosphate of Potash, $2KO + PO^5$ (fused), is obtained by mixing an alcoholic solution of potash with phosphoric acid, adding so much alcohol that the liquid becomes milky, evaporating to dryness the acid syrup, which subsides in the course of twenty-four hours, heating it to redness, and exhausting the ignited residue with water. The syrupy deposit from the alcoholic liquid is a mixture of $2KO, HO + PO^5$ with $KO, 2HO + PO^5$. On ignition these two salts are converted into a mixture of pyrophosphate and metaphosphate of potash, the latter of which is insoluble in water. The pyrophosphate of potash may therefore be easily separated from the metaphosphate. In the ignited state the pyrophosphate of potash forms a white fused mass, which rapidly deliquesces in the air; its solution in water has an alkaline reaction, and may be boiled without being converted into the ordinary phosphate. On analysis of the fused salt the author obtained—

KO.....	56·71	2 =	94·4	56·93
PO^5	42·71	1	71·4	43·07

The syrupy solution of the pyrophosphate of potash solidifies, on evaporation over sulphuric acid, to a white radiating mass, which on drying below 212° parts with 1 atom, and on ignition with 3 atoms of water; so that the composition of this salt is $2KO + PO^5 + 3HO$. At 356° this compound lost 9·8 per cent. of water; the calculated loss, corresponding to 2 atoms of water, amounts to 9·79 per cent.

This salt, $2KO + PO^5 + HO$, which is formed at 356°, is not converted into phosphate; it precipitates nitrate of silver white. The third atom of water does not escape below 572°; at this temperature the loss of water of the salt $2KO + PO^5 + 3HO$ amounted to 14·05 per cent.

Bipyrophosphate of Potash, $KO, HO + PO^5$.—From a solution of the neutral potash salt in acetic acid alcohol precipitates the acid pyrophosphate in the form of a syrup, while acetate of potash remains dissolved in the alcohol. The syrup is placed over sulphuric acid, when it solidifies in the course of a few days. The salt is white and deliquescent; its solution has an acid reaction, and may be boiled without alteration. According to analysis it has the following composition—

KO.....	37·14	1 =	47·2	36·99
HO	7·13	1	9·0	7·05
PO^5	55·73	1	71·4	55·96

Pyrophosphate of Potash and Oxide of Ammonium, $2KO + PO^5 + NH^4O, HO + PO^5 + HO$, obtained by supersaturating biphosphate of potash with ammonia, and evaporating over a mixture of chloride of ammonium and caustic lime, forms a white deliquescent salt with an alkaline reaction, which parts with ammonia on boiling, and is reconverted into the bipyrophosphate of potash. After precipitation with nitrate of silver the liquid above the white precipitate has an acid reaction. Analysis gave—

KO.....	33·65	2 =	94·4	33·56
NH^3	6·61	1	17·0	6·04
HO.....	9·33	3	27·0	9·60
PO^5	50·41	2	142·8	50·80

Pyrophosphate of Soda, $2NaO + PO^5 + 10HO$, obtained by heating to redness the ordinary phosphate of soda, forms while hot a colourless glass, which becomes on cooling opake and uneven. It is less soluble in water than the ordinary phosphate; it lost on ignition, after having been dried at 248°, 0·3 per cent. According to Blucher, it parts with its water over sulphuric acid, but again absorbs it in a moist atmosphere. Stromeyer states that it is converted into the ordinary salt by boiling with mineral acids.

Bipyrophosphate of Soda, $NaO, HO + PO^5$, was obtained by dissolving neutral crystallized or fused pyrophosphate of soda in acetic acid and the addition of alcohol, in the form of a white crystalline powder, while the alcohol held in solution acetate of soda. The solution of the salt has an acid reaction, can be boiled without experiencing any change, and gives a white precipitate with nitrate of silver. The following results were obtained on analysis:—

NaO	27·50	1 =	31·2	27·95
HO	8·43	1	9·0	8·07
PO^5	63·15	1	71·4	63·98

When the ordinary phosphate of soda is dissolved in nitric acid, and alcohol added, no pyrophosphate is formed; but the biphosphate of soda, $NaO, 2HO + PO^5$, which separates in a crystalline form.

Pyrophosphate of Soda and Potash, KO, NaO + PO^5 + 12HO, is obtained by saturating the preceding acid salt of soda with carbonate of potash, and evaporating to a syrup, when it separates in white transparent prisms, the solution of which has an alkaline reaction. When dried in the air it afforded on analysis—

KO.....	18·18	1 =	47·2	18·30
NaO	12·08	1	31·2	12·10
PO^5	27·64	1	71·4	27·71
HO	42·10	12	108·0	41·89

Pyrophosphate of the Oxide of Ammonium, 2NH^4O + PO^5, was obtained by supersaturating pyrophosphoric acid with ammonia and the addition of alcohol in crystalline laminæ. It does not form phosphate on boiling with water, but bipyrophosphate of ammonia, ammonia being expelled. Nitrate of silver affords a white precipitate with the solution of this salt, and the liquid above the precipitate is neutral. When heated with ammonia, however, phosphate is formed. The analysis of this salt gave—

NH^3	27·27	2 =	34·0	27·55
HO	14·97	2	18·0	14·58
PO^5	57·76	1	71·4	57·87

Bipyrophosphate of the Oxide of Ammonium, NH^4O, HO + PO^5, separates from the preceding neutral salt in acetic acid on the addition of alcohol as a syrup, which changes after some time into small nacreous crystals. The salt, freed from acetate of ammonia by means of alcohol, is readily soluble in water, and precipitates a solution of the nitrate of silver with elimination of half the nitric acid. Its solution can be boiled without the salt passing into phosphate. Analysis gave—

NH^3	17·24	1 =	17·0	15·98
HO.....	16·12	2	18·0	16·92
PO^5	66·64	1	71·4	67·10

Pyrophosphate of Soda and Ammonia, NaO, NH^4O + PO^5 + 5HO. —When a solution of the acid soda salt in water is saturated with ammonia, and the solution is then evaporated over a mixture of chloride of ammonium and burnt lime, this salt is obtained in white prisms, which are easily soluble in water, part with ammonia on boiling, and are again converted into the bipyrophosphate of soda. Analysis yielded—

NaO	17·70	1 =	31·2	17·97
NH^3	10·18	1	17·0	9·79
PO^5	40·55	1	71·4	41·12
HO	31·57	6	54·0	31·12

Pyrophosphate of Baryta, 2BaO + PO^5 + HO (dried at 212°), is obtained on precipitating pyrophosphate of soda with chloride of barium. Pyrophosphoric acid is precipitated by barytic water. The salt is an amorphous white powder, which is somewhat soluble in water, dissolves in mineral acids, but is insoluble in acetic acid and pyrophosphate of soda. It dissolves however in consider-

able quantity in pyrophosphoric acid. The salt, dried at 212°, lost on ignition 4·02 per cent. water. The ignited salt gave on analysis—

BaO.....	68·08	2 =	153·2	68·21
PO^5	31·92	1	71·4	31·79

Pyrophosphate of Strontia, 2SrO + PO^5 + HO (dried at 212°), falls as a white powder on mixing nitrate of strontia with pyrophosphate of soda; the precipitate becomes crystalline when the liquid is warmed. The crystals are white, somewhat soluble in water, easily so in mineral acids, but insoluble in acetic acid and in pyrophosphate of soda. The salt, dried in the water-bath, lost on ignition 4·76 per cent. water. On analysis of the dried salt, the author obtained—

SrO	59·22	2 =	104·0	59·29
PO^5	40·78	1	71·4	40·71

Pyrophosphate of Lime, 2CaO + PO^5, falls, on the addition of chloride of calcium to a solution of pyrophosphate of soda, as an amorphous white powder. When this is dissolved in water, saturated with sulphurous acid, and heated, the salt separates in a crystalline state as the sulphurous acid is expelled. A solution of the crystals gives a white precipitate with nitrate of silver. Both forms of the salt are somewhat soluble in water, readily so in mineral acids, but insoluble in acetic acid. Lime-water is precipitated by pyrophosphoric acid. The salt, dried at 212°, lost on ignition 9·44 per cent., that dried at 230°, 6·91 per cent. of water; the formula 2(CaO, PO^5) + 3HO requires 9·58, the formula 2CaO + PO^5 + HO 6·61 per cent. The ignited salt gave on analysis—

CaO....	43·77	44·68	43·59	2 =	56·0	43·96
PO^5	56·23	55·32	56·41	1	71·4	56·04

Pyrophosphate of Magnesia, 2MgO + PO^5 + 3HO (dried at 212°).—Sulphate of magnesia yields, when mixed with phosphate of soda, an amorphous precipitate resembling the hydrate of alumina, which shrinks like that on drying. When the salt is dissolved in sulphurous acid and boiled, it is obtained in the form of a crystalline powder. The salt dissolves somewhat in water, and entirely in mineral acids and in pyrophosphate of soda. After desiccation at 212°, it still parts with 20·64 per cent. water at a red heat. The formula given above requires 19·52 per cent. The ignited salt yielded on analysis—

	Amorphous.	Crystalline.			
MgO.....	35·61	35·8	2 =	40·0	35·9
PO^5	63·57	63·9	1	71·4	64·1

Pyrophosphate of Alumina, $2Al^2O^3$ + $3PO^5$ + 10HO (dried at 230°), is precipitated on mixing a solution of sublimed chloride of aluminum with one of pyrophosphate of soda. The liquid above the precipitate is neutral. The precipitate is amorphous, of a white colour, dissolves in pyrophosphate of soda and in aqueous sulphurous acid, and is again precipitated on boiling the latter solution. Neutral pyrophosphate of alumina dissolves in ammonia and in potash; but if the salt is first dissolved in muriatic acid, and then precipitated

with ammonia, the whole of the alumina falls, but a portion of its acid remains in the solution combined with ammonia. The neutral phosphate of alumina likewise dissolves in ammonia; but when it has been dissolved in muriatic acid, it is precipitated entirely by ammonia. The salt, dried at 230°, lost on ignition 22·78 per cent. of water; the above formula requires 22·11. The ignited salt furnished on analysis—

$Al^2 O^3$	32·52	2 =	102·8	31·43
PO^5	67·48	3	214·2	67·57

[To be continued.]

On Pinic and Sylvic Acids, and their Products of Decomposition. *By* A. Laurent.

Pinic and sylvic acids were first analysed by H. Rose, who assigned to them the formula $C^{40} H^{32} O^4$, their salts being represented by $C^{40} H^{32} O^4 + MO$. Subsequently M. Liebig showed that sylvic acid contains $C^{40} H^{30} O^4$; and, on the other hand, I have shown that pinic acid possesses the same formula.

Six or seven years ago, on examining the resin which exudes from *Pinus maritima*, in the neighbourhood of Bordeaux, I discovered in it a new acid, which I called pimaric acid, and which possesses the same composition as the preceding. Pimaric acid, distilled *in vacuo*, is converted into pyromaric acid without any change of composition; and lastly, this acid, crystallized and left to itself, experiences another isomeric modification, and is converted into amorphous uncrystallizable pimaric acid.

The salts of all these acids are represented by the following composition, $C^{40} H^{30} O^4 + MO$, which is not in accordance with the ideas entertained by M. Gerhardt and myself. These salts should contain either $C^{40} H^{29} O^3$, MO or $C^{40} H^{31} O^5$, MO. The salts examined by myself and Prof. Rose are those of silver and lead. As it would have been difficult, in analysing these salts afresh, to ascertain whether they contained HO more or less, I attempted to determine whether the preceding acids, in combining with anhydrous oxides, disengaged water or not. For this purpose I mixed some sylvic and pimaric acid in the state of powder with recently-fused litharge likewise pulverized. The mixture was heated in a glass exsiccator, in a current of dry air; a little water was disengaged, but the quantity did not correspond to more than one-third of an atom. Presuming that the contact of the acid and of the oxide was not sufficient, I poured upon the mixture a little æther, and then heated it to 284°. 1·000 grm. of pimaric acid lost on fusion 0·028 of water.

1·00 of sylvic acid lost on fusion 0·034 of water.

1·000 grm. of pimaric acid, when heated alone to 284°, experienced a loss of 1 milligrm.

1·00 grm. of sylvic acid, when heated alone to 284°, experienced a loss of 2 milligrms., according to the formula $C^{40} H^{29} O^3$, HO. The loss ought to be near upon 3·00. The salts which should form ought to be represented by $C^{40} H^{29} O^3$, MO.

In treatises on chemistry it is stated that sylvic acid crystallizes in four-sided tablets. As pyromaric acid crystallizes in triangular tablets, the acid I have obtained differs from the preceding. Having had occasion to see some sylvic acid, I found it to possess the same form as pyromaric acid; and M. Mitscherlich, to whom I showed a sample of the latter, equally recognised it from its remarkable form to be sylvic acid.

Pimaric acid is the natural acid which exudes from *Pinus maritima*. When heated, to separate from it the oil of turpentine, a resin remains, which is generally a mixture of pimaric and sylvic acids. With respect to the amorphous pimaric acid, it is possible that it may be identical with pinic acid, if indeed this is really uncrystallizable from alcohol. It will therefore be requisite to examine the resins which exude from the other species of pines, to ascertain whether they contain pimaric or sylvic, or whether this latter is not a product resulting from the action of heat upon the first. With regard to pinic acid, it must equally be seen whether it exists in the fresh resin of the pine or whether it is derived from a modification of pimaric acid.

I shall call to mind that crystallized pimaric acid is converted, in the course of time, into amorphous or pinic acid; while the acid which has been melted experiences no modification. When the pimaric acid is very pure, a portion of it may crystallize after having been fused; if a dozen of grammes be used, it assumes the granulated appearance of sugar; when a smaller quantity is operated upon, it remains transparent and vitreous on cooling. I have shown that the acid crystallized from alcohol dissolves in about 10 times its weight of this liquid; whilst the same acid, which has been fused and powdered, dissolves instantly in its volume of alcohol; but that it separates almost immediately, returning to the crystalline modification soluble in 10 parts of alcohol. Pimaric acid, crystallized by fusion, behaves in nearly the same manner towards alcohol as the acid crystallized from that liquid.

Nitromaric Acid.—I obtained this by treating pimaric acid for a considerable length of time with boiling nitric acid; I have repeated the experiment, maintaining the ebullition for only seven or eight minutes. The product, washed with water, dissolved in alcohol, and reprecipitated by water, afforded on analysis nearly the same numbers as those previously obtained:—

Carbon	57·2	57·0	40 =	3000	56·87
Hydrogen	5·6	5·9	26	325	6·15
Nitrogen	7·2	7·1	2	350	6·60
Oxygen	30·0	30·0	16	1600	30·38

This acid is yellow, amorphous, resinous and insoluble; it softens, and is decomposed at its fusing-point. Its ammoniacal salt, which is very soluble, may be dried in transparent orange-red laminæ. The lead salt, which is slightly soluble in alcohol, contained 32·8 and 33·4 lead, and is represented by the formula $C^{40}\,H^{24}\,N^{2}\,O^{12}\,4PbO$. As the lead salt deflagrates slightly when heated and the nitromarates are yellow, the nitrogen must exist in the state of hyponitric acid,

$NO^4 = X$; then nitromaric acid becomes $C^{40}\,H^{36}\,X^2\,O^8$, being derived from $C^{40}\,H^{28}\,O^8$.

Compared with pimaric acid.....	$C^{40}\,H^{30}\,O^4$, monobasic,
we have maric acid	$C^{40}\,H^{29\frac{1}{2}}\,O^8$, bibasic,
nitromaric acid	$C^{40}\,H^{26}\,X^2\,O^8$, bibasic.

It is seen that under the influence of nitric acid pimaric acid first exchanges H^2 for O^2, then absorbs 2 other atoms of oxygen, becoming the bibasic maric acid (unknown); this subsequently exchanges H^2 for its equivalent X^2, and is converted into nitromaric acid.—*Ann. de Chim. et de Phys.*, 1848.

ANALYTICAL CHEMISTRY.

Note on a Reagent for Strychnine. By E. Marchand.

In 1843 M. Marchand described the remarkable and perfectly characteristic property possessed by strychnine of giving a magnificent blue colour, passing quickly to violet, and lastly to yellow, when triturated with peroxide of lead, and a few drops of concentrated sulphuric acid, containing $\frac{1}{100}$dth of its weight of nitric acid. Since the period above-mentioned several chemists have examined this reaction, and M. Herzog has proposed to omit the nitric acid as useless; another chemist proposes to substitute peroxide of manganese for peroxide of lead, and M. Otto prefers bichromate of potash to these oxides, which, according to him, gives rise to a much finer violet colour, and to a certain extent this is certainly the case.

M. Marchand proposes certain objections to these omissions and substitutions, and demonstrates that the reagents which he has proposed are the best suited to the purpose.

First, the nitric acid added in the proportion of $\frac{1}{100}$dth to the sulphuric acid is not useless, as stated by M. Herzog; for by its influence the series of colours is produced much more readily and sensibly than when it is omitted. M. Marchand states that he was aware that strychnine yielded a fine blue colour by the action of pure sulphuric acid and peroxide of lead only; but that it is almost impossible to perceive the red and yellow colours, which are readily perceptible in the conditions described by him: and the author adds that he never said or believed, as supposed by M. Herzog, that strychnine, when placed in the circumstances described, might serve as a reagent for nitric acid.

As to the substitution of peroxide of manganese for that of lead, the author has only one objection to make, which is that the salts of manganese sometimes possessing a red colour, there can be no certainty that the series of colours obtained belongs properly to the substance supposed to be strychnine, since one of the reagents employed may itself give rise to one of the colours indicated.

The same is the case with the bichromate of potash recommended by M. Otto. This salt produces by its solution in sulphuric acid a

yellow or green colour, and it follows that the series of colours indicated by M. Marchand is diminished by at least one colour, and sometimes by two, the yellow and the red, and consequently the reaction is far from being complete.

The method of employing M. Marchand's process is that of triturating the strychnine with peroxide of lead and concentrated sulphuric acid containing 1 per cent. of nitric acid; by this process the colours obtained are blue, becoming rapidly violet, then gradually red, and lastly, after some hours, it assumes a delicate yellow colour.—*Journ. de Pharm.*, Avril 1848.

On a simple Method of distinguishing the Red Flame of Lithia from that of Strontia by the Blowpipe. By Edward J. Chapman*.

If, on exposing a fragment of any substance to the action of the blowpipe, the flame assume a decided red colour, we may conclude with perfect safety that either lithia or strontia is present; for the tint produced under certain circumstances by lime is far too weak and faint to be considered characteristic, or to be placed for a moment in comparison with that obtained by the former bodies. The question therefore is, presuming that a red flame be obtained, to which of these two bodies is the coloration due?

Plattner remarks, without however following up the subject or turning it to any account, that the presence of chloride of barium prevents chloride of strontium from imparting a crimson tint to the flame; and this reaction may be employed, I have found, successfully, and in all cases, to distinguish lithia from strontia. For this purpose, a small quantity of chloride of barium must be fused at the bent end of a platinum wire, and a fragment of the substance under examination being added to it, the whole is to be exposed to the point of the inner flame, when, if lithia be present, a fine red colour will be produced; but, on the contrary, if this red tint do not appear, we may be certain that the former coloration, in the treatment of the substance *per se*, was due to strontia.

In the mineral kingdom, the *strontianite* and *celestine*, the silicates *lepidolite*, *spodumene*, &c. offer ready examples for the verification of this test.

Chloride of barium by itself imparts an apple-green tint to the flame; but this, on the addition of strontia, is converted into an impure yellow colour, somewhat resembling that produced by soda.

In the fusion of substances containing lithia with chloride of barium, the red colour of the flame is rendered far more intense. This is particularly seen with the *triphylline*, a phosphate of the protoxides of iron and manganese with lithia, &c., which alone colours the flame chiefly green, owing to the phosphoric acid it contains; but which, when treated with the above reagent, and especially when exposed with it to comparatively a feeble degree of heat, imparts to the surrounding flame a beautiful crimson hue.

* Communicated by the Author.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Mellitic Acid. *By* Profs. ERDMANN *and* MARCHAND.

LIEBIG and Wöhler formerly advanced the formula $C^4 O^3$ for mellitic acid; subsequently Liebig and Pelouze, in consequence of an amount of water found in the silver salt dried at 212°, adopted the formula $C^4 O^4 H$ for this acid as contained in the salts dried at 212°; whilst the same chemists found for the somewhat blackened silver salt dried at 356° the same composition, $C^4 O^4 Ag$, as Liebig and Wöhler had previously arrived at for the mellitate of silver. According to the researches of the authors, the older formula of Liebig and Wöhler for mellitic acid, $C^4 O^3$, is the correct one. With respect to the preparation of the salts described in the following pages, it may be observed in general that the insoluble mellitates cannot be obtained in a pure state by precipitating the solutions of different salts with that of the mellitate of ammonia; they were all found to contain ammonia. To prepare pure mellitic acid, the ammonia salt was boiled with an excess of baryta, the baryta separated with sulphuric acid, and the acid purified from adherent sulphuric acid by recrystallization.

Mellitate of Silver, AgO, $C^4 O^3$, forms a scaly, crystalline, shining powder, which appears under the microscope to consist of quadratic tablets with the angles generally truncated. The salt explodes gently when heated; it experiences no alteration up to 356° when pure; but the silver salt prepared by precipitating nitrate of silver with mellitate of ammonia always contains some ammonia, and such a salt becomes black at an elevated temperature. This behaviour was probably the reason why Liebig and Pelouze subsequently advanced the formula $C^4 O^4 H$ instead of the old one $C^4 O^3$, which is now confirmed. The authors never obtained more than 1 per cent. of water on combustion of the silver salt, while if the salt contained only 1 equiv. of water, this would give more than 5 per cent. In the examination of a salt which had been prepared in the manner above described, it was found that the water obtained on combustion was derived from a small amount of ammonia and water, which most tenaciously adhered to it. The salt precipitated by free mellitic acid from the acetate or nitrate of silver was, with the exception of a trace of water, perfectly pure. It afforded on combustion, after being dried at 266°, 0·7 per cent. water and 14·53 per cent. of car-

bon. Deducting the water found in the analysis as not essential, the results are—

Carbon	14·40	14·70	14·68	14·65	4	14·63
Oxygen	14·45	..	..	..	3	14·63
Oxide of silver	71·15	..	..	..	1	70·74

Mellitate of Lead, PbO, $C^4 O^3$ (at 356°), was prepared by precipitating acetate of lead with pure mellitic acid. This salt likewise tenaciously retains a small amount of water. It experiences no apparent alteration at 356°. After deducting 2·3 per cent. water, which was found on analysis, and which is certainly not essential, since the formula PbO, $C^4 O^3$ + HO requires 66·18 per cent. oxide of lead and 5·81 water, the results stand as follows:—

Carbon	14·57	4	15·04
Oxygen	15·43	3	15·04
Oxide of lead	69·74	1	69·92

Mellitate of Soda, NaO, $C^4 O^3$ (at 310°).—This salt is obtained from cold saturated aqueous solutions on evaporation in large, strongly striated and very imperfectly formed crystals, which contain 38·88 per cent. or 6 atoms water of crystallization; the crystals have a faint lustre of mother-of-pearl. From hot saturated solutions, broad, thin, acicular crystals separate, which lost at 212° 22·6 per cent., or 3 equivs. water. At 356° the total loss of water amounted to 32·81 per cent., which corresponds to 4 equivs. The salt, dried at 310°, contained 38·68 per cent. of soda. The formula given above requires 39·22.

Neutral Mellitate of Potash, KO, $C^4 O^3$ + 3HO, is isomorphous with the corresponding salt of ammonia; it was obtained anhydrous at 338°, as the following numbers show:—

					Amount of water in the crystalline salt.	
					Found.	Calculated.
Mellitic acid ..		1 =	600·0	50·46		
Potash	49·51	1	588·9	49·54	20·1	22·1

Acid Mellitate of Potash, 2KO + $3C^4 O^3$ + 9HO (crystallized), is precipitated on the addition of free mellitic acid to a concentrated solution of the preceding neutral salt, in the state of a fine crystalline powder. When collected and dissolved in water, it separates in minute broad crystals with a mother-of-pearl lustre, which constitute a sesquiacid salt. Analysis gave—

Potash	30·49	2 =	1177·8	29·51
Mellitic acid ..		3	1860·0	45·08
Water	24·65	9	1012·5	25·37

Neutral Mellitate of Ammonia, $NH^4 O$ + $C^4 O^3$ + 3HO (crystallized), effloresces, but cannot be freed entirely from water of crystallization by the application of heat, because it begins to part with ammonia at 212°. When dissolved in water, and ammonia is added to it, it falls as a fine powder, which however subsequently unites into well-developed crystals. The pulverulent precipitate and the

crystals have the same composition. Sometimes the crystals keep for a long time unaltered, but in general they soon become dull and porcelaneous, experiencing a loss of water amounting nearly to 1 equiv. The crystallized salt gave on analysis—

Carbon.....	24·12	4 =	300·0	23·76
Hydrogen ..	7·09	7	175·0	6·93
Nitrogen	14·14	1	87·5	13·86
Oxygen	54·65	7	700·0	55·45

Trimellitate of Ammonia, $NH^4O + 3C^4O^3 + 6HO$ (crystallized).—The crystals belong to the rhombic system. It has been stated above that all the insoluble salts of mellitic acid which are precipitated by the decomposition of different salts with mellitate of ammonia contained ammonia. On decomposing the precipitate formed on the addition of sulphate of copper to a solution of mellitate of ammonia with sulphuretted hydrogen, and evaporating the filtered liquid, the trimellitate of ammonia was obtained.

Mellitate of Copper.—Acetate of copper, precipitated with free mellitic acid, forms at first a stiff jelly, which is converted, after a considerable time and on drying, into crystals. On precipitating a neutral salt of copper with mellitate of potash, a salt is obtained, which it is impossible to free entirely from potash. The salt obtained by the first method is an acid salt, which is represented in the crystalline state by the formula $CuO, 3C^4O^3 + 12HO$. When a boiling solution of acetate of copper is mixed with mellitic acid, the neutral salt $CuO, C^4O^3 + 4HO$ separates in a flocculent state, but likewise becomes crystalline on washing. The air-dried salts afforded on analysis—

		Acid salt.				Neutral salt.			
Oxide of copper ..	25·51	2=	993·2	23·97	32·48	1 =	496·6	32·12
Mellitic acid	42·12	3	1800·0	43·44	38·84	1	600·0	38·79
Water	32·39	12	1350·0	32·59	29·04	4	450·0	29·09

Mellitate of Copper and Ammonia, $3(CuO, C^4O^3, HO) + NH^4O, C^4O^3 + 15HO$ (crystallized).—This is the compound mentioned above, from which the trimellitate of ammonia was prepared. It forms beautiful sky-blue crystals. The salt dried at 230° contains $3CuO, NH^3, 4C^4O^3, 4HO$. According to this formula, on decomposing the salt with sulphuretted hydrogen, 1 equiv. mellitic acid should be set free along with the trimellitate of ammonia. The analysis of the hydrated salt furnished 23·2 per cent. oxide of copper and 39·2 per cent. water; the first formula requires 23·87 per cent. CuO and 39·66 HO. The analysis of the salt dried at 230° yielded 31·9 per cent. oxide of copper and 5·08 ammonia; the second formula requires 32·72 and 4·66.

Mellitates of Lime and Baryta are both very difficult to dry, but they appear to be anhydrous. When prepared from the mellitate of ammonia by double decomposition, they always contain traces of ammonia.

Mellitovinic Acid, $C^4H^5O, 2C^4O^3$ (formula of the acid contained

in the baryta salt), is obtained on long-continued boiling of mellitic acid containing sulphuric acid with alcohol. On saturating with baryta, sulphate and mellitate of baryta separate; the filtered liquid is exposed to the air to remove the excess of baryta, filtered, and dried over sulphuric acid. This salt forms a gummy mass, which rotates upon water like the butyrate of baryta, yielding a clear solution; metallic salts produce no precipitates in its solution. It is decomposed at 212°, and then leaves a residue of carbonate of baryta on solution in water. The following numbers, deduced from the analysis of the baryta salt, are compared with the calculated numbers:—

Carbon	34·02	12 =	900·0	34·34
Oxygen	26·83	7	700·0	26·72
Hydrogen	2·58	5	62·5	2·38
Baryta	36·57	1	958·0	36·56

Journ. für Prakt. Chem., xliii. p. 129.

On the Composition of Human Milk.
By J. W. Griffith, M.D., &c.*

The object of the present paper is merely to communicate the results of some ultimate analyses of the human milk. This secretion has been frequently analysed proximately, but not I believe ultimately; which is perhaps somewhat singular, since its great importance as being the natural type of our food, at least at one period of life, must render its investigation in every point of view of interest.

The analyses were made by drying the fresh milk at 212° F., burning it with chromate of lead, &c. The nitrogen was determined by Varrentrapp and Will's method, excepting where otherwise stated.

The subjects from whom the milk was derived were all healthy.

I. Taken fourteen days after parturition; meat and beer being among the articles of food. It yielded 12·49–12·58 per cent. of solids.

Dry extract. 6·055 grs. gave 11·23 carbonic acid and 4·29 water; 7·805 gave 2·36, and 5·15 gave 1·58 ammonio-chloride of platinum; 1·61 gave 0·025 ash. These quantities correspond to—

	I.	II.
Carbon	50·57	
Hydrogen	7·86	
Nitrogen	1·90	1·92†
Oxygen	38·12	
Ash	1·55	
	100·00	

* Communicated by the Author.

† The determination of the nitrogen in milk requires much care, in consequence of the large amount of hydrocarbons which contaminate the hydrochloric solution of ammonia and reduce the platinum. I found it to succeed best when the solution was evaporated gently to about half its bulk before the addition of the chloride of platinum; notwithstanding this precaution, some of the platinum is almost

II. The milk of a poor woman, living entirely upon vegetable food. Specific gravity, 1030. Solids at 212° F. = 13·62 per cent. one month after parturition.

α. 3·99 gave 7·335 carbonic acid and 2·78 water; 8·93 gave 0·135 ash. The nitrogen was not determined.

β. From the same person, two days subsequently. 4·88 gave 8·96 carbonic acid and 3·385 water; 6·515 gave 0·10 ash, corresponding to—

	α.	*β.*
Carbon	50·13	50·08
Hydrogen	7·73	7·70
Nitrogen and Oxygen	40·63	40·69
Ash	1·51	1·53

III. One month and fourteen days after parturition; mixed diet. Solids = 12·87 per cent. 12·21 of the extract gave 0·22 ash; 7·93 gave 15·01 carbonic acid and 5·64 water; 8·23 gave 2·579 ammonio-chloride of platinum, corresponding to—

Carbon	51·61
Hydrogen	7·90
Nitrogen	1·96
Oxygen	36·74
Ash	1·80

IV. Nine months and six days after parturition; mixed diet. Specific gravity, 1028. 3·665 of the extract gave 0·065 ash; 3·64 gave 6·27 carbonic acid and 2·415 water; 4·67 gave 1·47 ammonio-chloride of platinum, corresponding to—

Carbon	46·97
Hydrogen	7·39
Nitrogen	1·97
Oxygen	41·90
Ash	1·77

V. Ten months after parturition; mixed diet. Specific gravity, 1034. 4·38 extract gave 8·09 carbonic acid and 3·195 water; 4·320 gave 7·96 carbonic acid and 3·02 water; 3·23 gave 0·06 ash; 7·04 gave 0·15 ammonia, and 5·82 gave 1·67 ammonio-chloride of platinum, corresponding to—

always reduced, so that the ammonio-chloride must be subsequently washed out of the filter with water, and the weight of the filter, &c. deducted from its original weight when containing the platinum salt. The error which would occur without this precaution is shown by the following facts:—The amount of nitrogen in the above analyses, calculated from the increase in weight of the original dried filter, considering the whole of its contents after washing with the mixture of æther and alcohol as ammonio-chloride of platinum, amounted to 2·22–2·28 per cent.; after washing with water, to 1·90–1·92. The insoluble portion in each case contained reduced platinum, as shown by dissolving it in nitromuriatic acid and adding ammonia, when the ammonio-chloride crystallized readily.

	I.	II.
Carbon	50·36	50·23
Hydrogen	8·10	7·75
Nitrogen	1·75*	1·80
Oxygen	37·94	
Ash	1·85	

VI. The milk of a scrofulous and phthisical young woman, ten months and a half after parturition; mixed diet. The milk was evidently poor in solids and in butter; it had a bluish aspect (on which account it had been sent me for examination). This colour did not arise from the presence of any colouring matter, but depended upon the diminished number of globules.

Of the extract, 6·66 gave 10·58 carbonic acid and 4·64 water (the nitrogen was not determined), corresponding to—

Carbon	43·31
Hydrogen	7·80
Nitrogen and Oxygen	46·98
Ash	1·91

Hence the milk appears richer in carbon and hydrogen during the earlier periods of lactation, whilst the quantity of nitrogen undergoes but little variation†. The latter statement is not in accordance with the results obtained by Simon on the proximate analysis of the milk at different periods; he found that the proportion of caseine increased towards the later periods; but the process he adopted is probably not free from fallacy‡. Since caseine dried at 212° F. contains 15·9 per cent. of nitrogen, 2 per cent. of this element would correspond to 12·5 of caseine per cent. of the solid extract. The average amount of extract is 11·0 per cent. of the milk; this is stated to contain on the average 3 parts of caseine, or 27·2 per cent., which would correspond to 4·3 per cent. of nitrogen in the solid extract, whereas the average amount obtained is rather less than 2 per cent. (and that found by Schlossberger still less). Hence there appears an inconsistency between the results of the proximate and ultimate analyses of this fluid. The amount of caseine obtained by proximate analysis varies considerably according to the method adopted. When the butter is removed by æther, and the sugar and extractives by water, the proportion of caseine found is considerably less than when the sugar, &c. are removed by alcohol. The former method however gives results which are far more nearly in accordance with those obtained by ultimate analysis than the latter. Pro-

* In this analysis the ammonia formed by the combustion of the extract with the mixture of soda and lime was absorbed by sulphuric acid.

† Schlossberger found 1·5 per cent. of nitrogen, but the period at which the milk was taken is not stated.

‡ There is no question that the chemical properties of caseine are not always the same; for after desiccation, &c. this substance is sometimes more, at others less soluble in spirit or water. This probably depends upon the quantity and the nature of the saline matters present.

bably Haidlen's process is the best; but the separation of the butter to the surface during evaporation, and its adhesion to the walls of the evaporating dish, give rise to uncertainty, for it is very questionable whether the whole can be subsequently perfectly mixed.

With the view of comparing the results of the proximate and ultimate analyses of the same specimens of the extract, I made some by both methods.

Thus I., analysed by Haidlen's method, yielded—

Butter	25·56
Sugar and extractives	61·76
Caseine	12·68

From II. the butter was removed by æther, and the sugar, &c. by water; it yielded—

Butter	34·32
Sugar, &c.	52·41
Caseine	13·27

IV. was analysed in the same manner as the last, and yielded—

Butter	16·90
Sugar, &c.	76·60
Caseine	6·42

Calculating the whole of the nitrogen as derived from caseine (which is not strictly correct, although the amount of nitrogenous extractives is too small to interfere materially), and assuming the ultimate analyses as the bases, I. should have yielded proximately 2·03 per cent. of nitrogen, II. 2·172, and IV. 1·02. The two former correspond; but the latter does not, which probably depends upon the cause stated in the note.

In conclusion, I should wish to offer the *suggestion*, whether the secretions of the body (excluding the water and fat entering into their composition) are not really of two distinct kinds, viz. one in which the composition is uniform and constant, as the bile and milk; the other, in which the composition is variable and inconstant, from the exercise of a compensating or balancing function with some other secretion of the same kind, as exemplified in the urine and perspiration.

On Cyanuric Æther and the Cyanurate of Methylene.
By A. Wurtz.

Cyanuric æther is obtained by distilling in an oil-bath alkaline cyanurate of potash with sulphovinate of potash. The product condenses in the neck of the retort and the receiver to a crystalline mass, which is purified by dissolving it several times in alcohol, from which it separates on cooling in very brilliant prismatic crystals. The pure æther melts at 185° F. to a colourless liquid heavier than water; it boils at 529°, and may be distilled without experiencing the least alteration. The density of the vapour was found to be 7·4 = 4 vols.; calculation indicates 7·37. This density of vapour,

and the elementary analysis which I have made of the cyanuric æther lead to the formula $C^6 N^3 O^2, 3C^4 H^5 O$. It is slightly soluble in water, and dissolves readily in alcohol and ordinary æther. When boiled for any length of time with an alcoholic solution of potash, there is a constant disengagement of ammonia, while carbonic acid combines with the potash. In this case the regenerated cyanuric acid experiences the same kind of decomposition as the isomerous cyanic acid:—

$$C^6 N^3 O^3, 3C^4 H^5 O + 12HO = 6CO^2 + 3NH^3 + 3C^4 H^6 O^2.$$

When sulphovinate of potash is distilled with dry cyanate of potash, an extremely irritating liquid collects in the receiver, consisting of a mixture of cyanic and cyanuric æther. These two products are separated by distillation; the boiling-point of cyanic æther being at 140°, is first volatilized. I shall describe the remarkable properties of this new compound on another occasion. With respect to the cyanuric æther, which forms the residue of the distillation, it may easily be purified by frequent crystallization from alcohol. I have even observed that the crystals obtained in this manner are far more beautiful and regular than those procured by the process first described.

I obtained the cyanurate of methylene by distilling the cyanurate or the cyanate of potash with sulphomethylate of potash. Purified by frequent recrystallization from alcohol, the cyanurate of methylene exhibits the form of minute, colourless, prismatic crystals, which melt at 284° and volatilize at 563°. The density of the vapour of this æther was found to be 5·98, equal to 4 vols.; theory gives 5·94. The analysis which I have made of this body and the density of its vapour lead to the formula $C^6 N^3 O^3, 3C^2 H^3 O$; there is no doubt therefore that cyanuric acid is a tribasic acid, and that its constitution is expressed by the formula $C^6 N^3 O^3, H^3 O^3$, which M. Liebig assigned to it some ten years ago. This conclusion, which necessarily follows from my analyses, is of some importance, considering that Prof. Wöhler has recently published an examination of cyanuric acid to prove that it is bibasic*. If, as the majority of chemists conceive, the composition of an æther furnishes the safest means of determining the constitution of the corresponding acid, it appears to me that Prof. Wöhler's conclusions are invalidated by my experiments, and that the opinion adopted by Prof. Liebig should be retained.—*Comptes Rendus*, March 20, 1848.

On the Pyrophosphates. *By* Dr. A. Schwarzenberg.

[Continued from page 185.]

Pyrophosphate of Oxide of Chromium, $2Cr^2 O^3 + 3PO^5 + 7HO$ (dried at 266°), is obtained on precipitating crystallized chrome-alum with pyrophosphate of soda. This precipitate is of a dirty red colour when formed at the ordinary temperature, but of a light green colour from boiling solutions. The salt dissolves in pyrophosphate of soda and in aqueous sulphurous acid, from which solution

* Chem. Gaz., vol. v. p. 140.

it is again precipitated on boiling; it also dissolves in caustic potash. The salt, dried at 266°, lost on ignition 13·95 per cent. water; the formula given above requires 14·4; analysis furnished—

Cr^2O^3	41·46	2 =	160·0	42·76
PO^5	58·54	3	214·2	57·24

Pyrophosphate of the Protoxide of Manganese, $2MnO + PO^5 + 3HO$ (dried at 212°), is obtained by precipitating protosulphate of manganese with pyrophosphate of soda, as a white amorphous powder soluble in pyrophosphate of soda. It is decomposed by caustic potash. When dissolved in water containing sulphurous acid and boiled, it is obtained in beautiful nacreous laminæ. For analysis, it was dissolved in muriatic acid, precipitated with ammonia, and digested with hydrosulphate of ammonia. The sulphuret of manganese was dissolved in muriatic acid, and precipitated while boiling with carbonate of soda. The salt, dried at 212°, lost on ignition 16·54 per cent., and that dried at 248°, 6·0 water. The ignited salt gave on analysis—

MnO	50·15	2 =	72·0	50·2
PO^5	49·85	1	71·4	49·8

Pyrophosphate of Zinc, $2ZnO + PO^5$, obtained by precipitating sulphate of zinc with pyrophosphate of soda, forms a white, amorphous, voluminous mass, which shrinks on drying like the hydrate of alumina. When the powder is suspended in water, and sulphurous acid passed into it and boiled, it dissolves, and on cooling again separates as a heavy crystalline powder. If this crystalline powder is boiled with ordinary phosphate of soda, pyrophosphate of soda is obtained, which proves that the acid in the crystals is unaltered pyrophosphoric acid. Both the amorphous and crystalline salt are soluble in acids, caustic potash and ammonia; alcohol precipitates a syrupy mass from the solution in ammonia. The salt fuses in the outer flame of the blowpipe to a white globule, which becomes colourless in the inner flame without giving any considerable deposit of zinc. On heating the salt to redness in a current of hydrogen, a sublimate of metallic zinc and phosphorous acid is obtained, while phosphuretted hydrogen, easily recognised from the green flame with which it burns, is given off. A white mass is left, which contains phosphoric acid and oxide of zinc. The salt, dried at 212°, lost on ignition 8·44 per cent. of water; the formula $2(2ZnO + PO^5) + 3HO$ requires 8·17. The ignited salt furnished on analysis—

ZnO	54·17	1		53·46
PO^5	45·83	1		46·54

Pyrophosphate of Cadmium, $2CdO + PO^5 + 2HO$ (dried at 212°), falls as a heavy white powder on mixing a solution of sulphate of cadmium with one of pyrophosphate of soda; it is soluble in ammonia, pyrophosphate of soda and acids, but insoluble in caustic potash. On heating it to redness in a current of hydrogen, similar products are formed as with the zinc salt. It dissolves in sulphurous acid, and is again precipitated on boiling in nacreous laminæ. The

salt, dried at 212°, lost on ignition 8·99 per cent.; the above formula requires 8·28 per cent; the anhydrous salt afforded—

CdO.....	63·65	1 =	128·0	64·19
PO^5	36·35	1	71·4	35·81

Pyrophosphate of the Protoxide of Iron falls as a white amorphous precipitate on mixing a solution of the protosalt of iron with one of pyrophosphate of soda.

Pyrophosphate of the Peroxide of Iron, $2Fe^2O^3 + 3PO^5 + 9HO$ (dried at 230°), is obtained by dissolving sublimed perchloride of iron in water, and precipitating with pyrophosphate of soda. The liquid above the precipitate is neutral. The salt forms a very pale yellow powder, which becomes yellower at 212°, but after ignition again lighter. It dissolves in acids, ammonia and pyrophosphate of soda, but is insoluble in acetic and sulphurous acid and chloride of ammonium; when dissolved in muriatic acid without boiling and precipitated with ammonia, the precipitate dissolves entirely in an excess of ammonia, and behaves in this respect like the salt of alumina. Carbonate of ammonia dissolves it to a colourless liquid, while phosphate of iron dissolves in this medium with a yellow colour. It is imperfectly decomposed on fusing it with carbonate of potash and soda. The salt, dried at 230°, lost on ignition 17·66 per cent. of water; the above formula requires 17·95. The dry salt afforded—

Fe^2O^3	41·7	2 =	156·0	42·13
PO^5	58·3	3	214·2	57·87

When perchloride of iron containing muriatic acid is precipitated with pyrophosphate of soda, phosphate of iron is formed; on boiling it with phosphate of soda, no pyrophosphate is obtained, which is likewise proved by the following analysis:—The ignited salt contained 51·66 per cent. peroxide of iron and 48·34 phosphoric acid, corresponding to 1 atom of each constituent.

Pyrophosphate of Lead, $PbO + PO^5 + HO$ (dried at 212°), obtained by precipitating acetate of lead with pyrophosphate of soda, is an amorphous white powder, soluble in nitric acid, caustic potash and pyrophosphate of soda, but insoluble in ammonia, acetic and sulphurous acids. The salt, dried at 212°, lost on ignition 2·92; the formula given above corresponds to a loss of 2·95 per cent.; the anhydrous salt gave on analysis—

PbO.....	76·29	1 =	224·0	75·83
PO^5	23·71	1	71·4	24·17

Pyrophosphate of Nickel, $2NiO + PO^5 + 6HO$ (dried at 230°), obtained by precipitating sulphate of nickel with pyrophosphate of soda, is a light green powder, which turns yellow on ignition; it dissolves in mineral acids, pyrophosphate of ammonia and soda. If the nickel contained cobalt, alcohol only precipitates the cobalt compound from the ammoniacal solution, the salt of nickel remaining dissolved. By treatment with sulphurous acid the salt may be obtained in a crystalline state; if it contained cobalt, the cobalt com-

pound is first precipitated. The salt, dried at 230°, lost 26·05 per cent. of water. It gave on analysis—

NiO	51·3	2 =	55·0	51·23
PO^5	48·7	1	71·4	48·77

Pyrophosphate of Copper, $2CuO + PO^5 + 2HO$ (dried at 212°), is formed on precipitating a soluble salt of copper with pyrophosphate of soda. The salt is amorphous, greenish-white, blue at 212°, and light blue after ignition. It dissolves in mineral acids, ammonia and pyrophosphate of soda; boiling caustic potash decomposes it into oxide of copper and phosphate of potash. In one attempt to obtain the protosalt of copper by means of sulphurous acid, the crystallized salt of the oxide was obtained. The amorphous salt dissolved in sulphurous acid with a blue colour, without experiencing any change in its composition. Sulphurous acid has no reducing action upon the solution of the salt in ammonia; in general the amorphous salts dissolved in it are precipitated in a crystalline state on boiling. If some grape-sugar be added to the ammoniacal solution of this salt, a mixture of metallic copper and phosphate of the protoxide is obtained. On passing a current of sulphuretted hydrogen over the salt heated to redness, phosphuret of copper, $Cu^6 P$, a sublimate of phosphorous acid, phosphuretted hydrogen and water are obtained. The salt, dried at 212°, lost on ignition 11·28 per cent. of water. The above formula requires 10·62. On analysis the anhydrous salt gave—

	Amorphous.	Crystalline.		
CuO	52·1	52·89	2	52·84
PO^5	47·9	47·11	1	47·16

Pyrophosphate of Copper with Oxide of Copper and Ammonia, $3(2CuO + PO^5) + 2(CuO, 2NH^3) + 8HO$.—When the preceding salt is dissolved in ammonia, and alcohol added so that it does not mix with it, verrucous groups of crystals of this salt gradually separate. The crystals dissolve sparingly in water, and become brown when heated to redness; they were dried over a mixture of chloride of ammonium and caustic lime. On analysis they afforded—

CuO.....	46·76	8 =	320·0	47·46
NH^3.....	11·39	4	68·0	10·08
PO^5	31·14	3	214·2	31·77
HO	10·17	8	72·0	10·69

Pyrophosphate of the Protoxide of Mercury, $2Hg^2O + PO^5 + HO$. —Pyrophosphate of soda precipitates from a solution of the protonitrate of mercury a heavy white crystalline powder, which is soluble in nitric acid. When heated to redness, it leaves metaphosphate of the peroxide of mercury. When recently precipitated, it dissolves in pyrophosphate of soda, and on boiling the solution a black powder separates. When dried at 212°, it is no longer soluble in pyrophosphate of soda, but turns black in it. The dry salt afforded on analysis—

Hg^2O	83·45	2	83·45
PO^5	16·55	1	16·55
HO		1	

Pyrophosphate of the Peroxide of Mercury, $2HgO + PO^5$ (at 212°).—When a solution of the pernitrate of mercury is precipitated with pyrophosphate of soda, a white sediment is first formed, which subsequently turns yellowish-red; it is insoluble in pyrophosphate of soda, soluble in acids, and is decomposed by caustic potash. When boiled with phosphate of soda, pyrophosphate of soda is produced.

Pyrophosphate of Silver, $2AgO + PO^5$ (dried at 212°), is obtained by precipitating nitrate of silver with pyrophosphate of soda; the liquid remains neutral. It is white, soluble in nitric acid and ammonia, insoluble in pyrophosphates, and sparingly soluble in nitrate of silver. The salt, dried at 212°, lost on ignition 0·21 per cent. of water. It consisted of—

AgO	76·23	2 =	232·0	76·47
PO^5	23·77	1	71·4	23·53

When dissolved in ammonia and mixed with alcohol, colourless needles separate, which on exposure to the air part with ammonia.

Pyrophosphate of Bismuth is formed by adding pyrophosphate of soda to a solution of nitrate of bismuth mixed with acetic acid; the precipitate is white, amorphous and voluminous, but it is converted in the course of twenty-four hours into a heavy crystalline powder. Two distinct kinds of crystals were perceptible under the microscope. On boiling oxide of bismuth with the bipyrophosphate of soda, a considerable quantity of it is dissolved.

Pyrophosphate of Antimony.—When oxide of antimony is boiled with the acid salt of soda, a liquid is obtained which contains a large quantity of antimony in solution; evaporated over sulphuric acid, it dries to a cauliflower-like mass, which on digestion with water leaves the greater portion of the oxide of antimony undissolved.

White Phosphate of Silver, $2AgO + PO^5 + HO$ (dried over sulphuric acid).—The yellow phosphate of silver was dissolved in phosphoric acid and the solution evaporated over sulphuric acid, to obtain the white crystals described by Berzelius. No crystals separated when the solution had become quite syrupy; it was therefore mixed with æther, when so great an evolution of heat occurred that it began to boil. The white crystalline powder obtained was washed with absolute alcohol to free it from phosphoric acid. It is a white crystalline powder, which blackens by exposure to the light, and, as stated by Berzelius, is immediately decomposed by water into yellow phosphate of silver and free phosphoric acid. Analysis gave—

AgO	73·45	2	74·26
HO	3·03	1	2·88
PO^5	23·52	1	22·86

The salt lost 2·87 per cent. of water at 338°, and was entirely converted into pyrophosphate of silver, for now it was no longer decomposed by water; and it furnished, on boiling with phosphate of soda,

pyrophosphate. It is hence evident that water is requisite to the constitution of the phosphate of silver, that it cannot exist without this water, and that consequently phosphoric acid cannot be regarded as a bibasic acid.—Liebig's *Annalen*, Feb. 1848, p. 133.

An Examination of the Compounds of some Organic Bases with Sulphocyanic, Ferridcyanic and Ferrocyanic Acids. By C. Dollfus.

This investigation was made with a view of ascertaining the atomic weights of several organic bases. The amount of sulphocyanic acids in such compounds can be determined very accurately according to Will's observations upon the sulphocyanide of sinapine (sulphosinapine). For this purpose a weighed quantity of the compound is dissolved in water faintly acidulated with nitric acid, and precipitated with nitrate of silver; the sulphocyanide of silver formed is perfectly insoluble in the nitric acid, and can consequently be determined with great accuracy. With respect to the combinations of ferrocyanic and ferridcyanic acids with organic bases, they have hitherto never been submitted to analytical investigation.

I. *Sulphocyanides.*—This class of salts is obtained by saturating the alkaloids dissolved in alcohol with moderately dilute sulphocyanic acid. In case the salts which are formed are not so sparingly soluble that they immediately crystallize, the solution is evaporated over sulphuric acid. Some of the sparingly soluble compounds may be obtained directly by decomposition of the muriate, nitrate or sulphate of the organic base with sulphocyanide of potassium; but with several, for instance the sulphate of codeine, the compounds thus prepared contain potash, and may perhaps be double salts of the organic salt with cyanide of potassium.

Sulphocyanide of Morphine, $C^{34}H^{18}NO^6, C^2NS^2H + HO$ (dried at 194°), forms small, transparent, shining needles, which melt at 212°. 0·2234 grm. of the compound, dried at 194°, gave 0·1044 grm. of sulphocyanide of silver. Elementary analysis furnished 60·66 carbon and 5·80 hydrogen. The above formula requires 60·84 C and 5·63 H. The equivalent of the compound, calculated from the amount of sulphocyanide of silver found (H = 1), gives 955, and 296 as that of morphine. With this equivalent and the analyses already existing of morphine, we arrive at the composition—

Morphine	83·40	1	= 284	83·24
Water		1	9	
Sulphocyanic acid	16·60	1	59	16·76

According to this the formula for morphine is $C^{34}H^{18}NO^6$. The centesimal numbers, calculated in accordance with the above, agree very well with the results of the analyses of different chemists:—

	Liebig.		Regnault.		Will.	Laurent.		Calculated.
Carbon....	71·29	71·30	71·89	71·43	71·40	71·73	71·59	71·82
Hydrogen	6·33	6·34	6·86	6·84	6·72	6·59	6·63	6·33

The author consequently rejects those formulæ for morphine which contain more than 34 atoms of carbon. According to Laurent's formula, $C^{34}H^{19}NO^6$, the sulphocyanide should have yielded 5·95 per cent. hydrogen, while the author obtained only 5·80.

Sulphocyanide of Codeine, $C^{34}H^{19}NO^5, C^2NS^2H + HO$ (dried at 194°), is obtained, in the manner above described, in transparent needles, which melt at 212°; 0·2515 grm. gave 0·1179 grm. sulphocyanide of silver, from which we find the equivalent 353. Analysis afforded 62·30 per cent. carbon and 6·13 hydrogen. In connexion with existing analyses of pure codeine, these data lead to the following composition of the sulphocyanide:—

Codeine	83·32	1	= 277	82·95
Water		1	9	
Sulphocyanic acid	16·68	1	59	17·05

Hence the formula for pure codeine is $C^{34}H^{19}NO^6$. The centesimal numbers deduced from this formula agree with the results of former analyses:—

	Regnault.		Will.	Gregory.	Calculated.
Carbon	73·32	72·96	73·15	73·14	73·64
Hydrogen ...	7·23	7·19	7·25	7·23	6·86
Nitrogen	4·89		..	4·83	5·05

The formula $C^{34}H^{20}NO^5$ requires 73·38 per cent. carbon and 7·19 hydrogen. These numbers likewise approach very closely to the enumerated analytical results; but according to this formula the sulphocyanide of codeine should have yielded 6·36 per cent. hydrogen, while it furnished only 6·13.

Sulphocyanide of Brucine, $C^{46}H^{26}N^2O^8 + C^2NS^2H$, is easily soluble; it crystallizes from its solution in transparent plates, which are anhydrous, and do not melt at 212°. 0·7364 grm. afforded 0·2674 grm. sulphocyanide of silver, which gives 457 as the equivalent of the compound and 398 as that of pure brucine. On combustion it furnished 63·23 carbon and 6·13 hydrogen; hence the composition of the salt is—

Brucine	87·10	1	= 394	86·98
Sulphocyanic acid	12·90	1	59	13·02

This composition requires 63·57 per cent. carbon and 5·96 hydrogen. Hence the formula of brucine, determined from the sulphocyanide, is $C^{46}H^{26}N^2O^8$, which agrees with the results of former analyses:—

	Liebig.	Regnault.		Ettling and Varrentrapp.		Calculated.
Carbon	69·58	70·00	70·15	70·00	..	70·00
Hydrogen	6·66	6·88	6·67	6·75	..	6·64
Nitrogen	..	7·09	7·05	..	7·24	7·10

According to this, hydrated brucine is represented by the formula $C^{46}H^{26}NO^8 + 7HO$. This formula requires 13·78 per cent. of water; the quantity found amounts to 14·3. The chloride of bru-

cine and platinum, $C^{46}H^{26}N^{2}O^{8} + ClH + PtCl^{2}$, calculated according to this formula, requires 16·43 per cent. platinum; Varrentrapp and Will found 16·46, 16·59, 16·52 and 16·50.

Sulphocyanide of Strychnine, $C^{44}H^{24}N^{2}O^{4} + C^{2}NS^{2}H$, is somewhat sparingly soluble in water, and crystallizes in transparent needles. 0·2904 of the salt gave 0·1181 of sulphocyanide of silver, which gives 408 for the equivalent of the compound and 349 for that of strychnine. The salt, dried at 212°, furnished on combustion 67·70 per cent. carbon and 6·39 hydrogen, which numbers lead to the following composition:—

Strychnine	85·55	1 =	348	85·50
Sulphocyanic acid	14·45	1	59	14·50

This requires 67·81 per cent. carbon and 6·14 hydrogen; hence pure strychnine is represented by the formula $C^{44}H^{24}N^{2}O^{4}$. Of the existing analyses, that of Gerhardt, who arrived at the same formula, agrees most accurately with the numbers calculated according to this formula:—

	Liebig.	Regnault.		Gerhardt.	
Carbon	75·25	74·97	74·60	75·8	75·85
Hydrogen	6·70	6·69	6·86	6·9	6·80
Nitrogen	..	8·43	8·46	8·0	8·00

Sulphocyanide of Cinchonine, $C^{38}H^{22}N^{2}O^{2} + C^{2}NS^{2}H$, crystallizes in transparent brilliant needles, which contain no water. 0·5303 grm. gave, after drying at 212°, 0·2533 grm. sulphocyanide of silver; this gives 348 for the atomic weight of the compound, and 289 for that of cinchonine. It furnished on combustion 67·86 carbon and 6·63 hydrogen; according to these data its composition is—

Cinchonine.....	83·03	1 =	294	83·29
Sulphocyanic acid	16·97	1	59	16·71

which requires 67·9 carbon and 6·5 hydrogen. Laurent has shown that this formula for cinchonine, $C^{38}H^{22}N^{2}O^{2}$, agrees best with the numbers found for the salts of this alkaloid.

II. *Ferro- and Ferridcyanides.*—When an alcoholic solution of pure ferrocyanic acid, prepared according to Posselt's method*, is mixed with alcoholic solutions of the alkaloids, compounds of constant composition are obtained. Quinine and cinchonine, the only salts of this kind which the author has been able to investigate minutely, furnish orange- or lemon-coloured crystalline precipitates, which are very sparingly soluble in alcohol. Codeine gives a white precipitate, soluble in an excess of the acid, from which solution the salt crystallizes after a considerable time in minute white needles. Veratrine, morphine and brucine behave similarly; but these last compounds are so readily decomposed, that they cannot be recrystallized. When warmed, they are easily decomposed; both dry and in solution they part with prussic acid, and deposit white proto-

* Chem. Gaz., vol. i. p. 103.

cyanide of iron, which immediately turns blue. When heated to redness, the dry compounds leave pure peroxide of iron. Their aqueous solutions exhibit the reactions of ferrocyanic acid.

When the aqueous solution of the muriate of an alkaloid is mixed with an aqueous solution of ferridcyanide of potassium, compounds of ferridcyanic acid with the alkaloids are obtained in most cases. Muriate of quinine gives a pale yellow precipitate, which becomes crystalline when agitated, forming laminæ resembling *aurum musivum*; these salts are very sparingly soluble; in their preparation the solutions must not be too dilute. Cinchonine gives a yellow precipitate, consisting of acicular crystals; brucine, morphine and codeine furnish crystalline compounds only after a considerable time, and they are still more unstable than the corresponding ferrocyanides.

Ferrocyanide of Cinchonine, $C^{19}\,H^{11}\,NO + Cfy\,H^2 + 2HO$ (dried over sulphuric acid), or this formula doubled. The following numbers were obtained on analysis:—

Carbon	54·90	25 =	150	54·94
Hydrogen	6·10	15	15	5·49
Nitrogen	..	4	56	
Oxygen	..	3	24	
Iron	10·30	1	28	10·25

Ferridcyanide of Cinchonine, $C^{38}\,H^{22}\,N^2\,O^2 + Cfy^2\,H^3 + 4HO$ (dried at 212°), forms hard, acicular, lemon-coloured crystals. If the crystals have been dried at a low temperature, they experience no alteration at 212°. Their solution exhibits all the characters of ferridcyanic acid towards persalts and protosalts of iron. The salt furnished on analysis—

Carbon	55·22	50 =	300	55·04
Hydrogen	5·70	29	29	5·30
Nitrogen	..	8	112	
Oxygen	..	6	48	
Iron	10·34	2	56	10·27

The only difference between the ferridcyanide and ferrocyanide of cinchonine would, according to this, be that the former contains 1 atom less hydrogen to 50 atoms of carbon than the latter.

Ferrocyanide of Quinine, $C^{20}\,H^{12}\,NO^2 + Cfy\,H^2 + 3HO$, perfectly resembles the corresponding salt of cinchonine; it furnished on analysis—

Carbon	52·9	26 =	52·5	
Hydrogen	6·0	17	5·7	
Nitrogen	..	4		
Oxygen	..	5		
Iron	9·1	1	9·4	

Ferridcyanide of Quinine, $2(C^{20}\,H^{12}\,NO^2) + Cfy^2\,H^3 + 3HO$, forms laminæ resembling *aurum musivum* when precipitated from a cold concentrated, slightly-acid solution of muriate of quinine by a concentrated solution of ferridcyanide of potassium. It does not decrease in weight at 212°, dissolves readily in water, and is decomposed on

evaporating its solution. It contains, for 52 atoms of carbon, 1 atom less hydrogen than the ferrocyanide of quinine. The analysis of the salt, dried at 212°, gave—

Carbon	54·60	52 =	312	55·1
Hydrogen	5·46	30	30	5·3
Nitrogen.....	..	8	112	
Oxygen	..	7	56	
Iron.....	9·86	2	56	9·9

The following are the formulæ calculated by Dollfus:—

Morphine.....	$C^{34}H^{18}NO^6$	Brucine.....	$C^{46}H^{26}N^2O^8$
Codeine	$C^{34}H^{19}NO^5$	Strychnine ..	$C^{44}H^{24}N^2O^4$
or perhaps—		Cinchonine ..	$C^{38}H^{22}N^2O^2$
Morphine.....	$C^{34}H^{19}NO^6$	Quinine.....	$C^{20}H^{12}NO^4$
Codeine	$C^{34}H^{20}NO^5$		

It should be observed that the author has not hitherto succeeded in obtaining a sulphocyanide of quinine fit for analysis. Compounds of ferrocyanic acid with quinine and cinchonine were obtained; but the author does not look upon the analyses of them as decisive, from their being so very unstable. The above formula for cinchonine is based principally upon the sulphocyanide. Laurent's formula for quinine, $C^{38}H^{22}N^2O^4$, would alter the above-calculated formulæ for the ferrocyanide of quinine into $C^{38}H^{22}N^2O^3 + Cfy^2H^4 + 4HO$, which requires 53·4 per cent. carbon, 5·3 hydrogen, and 9·9 iron.—Liebig's *Annalen*, Feb. 1848, p. 212.

On the Estimation of Pyrophosphoric Acid, and on the Composition of the Phosphates of Lime. By M. Raewsky.

From the experiments and observations detailed in this memoir, it results:—

I. That pyrophosphoric acid may be estimated by the same process as that described by the author for phosphoric acid*, with this difference, that it must be precipitated by a solution of ammoniacal iron-alum, instead of by the neutral acetate of iron, as in the case of phosphoric acid.

II. That the artificial phosphate of lime, called by chemists bone phosphate, has the formula $PO^5, 3CaO$, instead of that assigned to it by Berzelius, $3PO^5, 8CaO$.

III. That the *natural* bone phosphate cannot have the same formula as that obtained artificially according to Berzelius's method; since certain bones, which are not pure phosphate, afforded on analysis more phosphoric acid than the so-called bone phosphate (admitting the formula $PO^5, 3CaO$).

IV. That the commercial biphosphate of lime is most frequently contaminated with phosphate of iron, of which it is easily purified. This salt is represented by the formula $PO^5, CaO, 2HO$, admitted by chemists.

V. That the biphosphate of lime is, as has been asserted, decomposed by alcohol into a phosphate of lime and free acid; but that

* See Chem. Gaz., vol. v. p. 241.

the isolated phosphate of lime is not, as supposed, a neutral salt, but a new phosphate represented by the formula $2PO^5, 3CaO, 4HO$.

VI. Lastly, that the phosphate obtained by the decomposition of chloride of calcium and phosphate of soda, varies in composition; the precipitate produced by pouring chloride of calcium into phosphate of soda possessing the formula $PO^5, 2CaO, 4HO$, while the salt derived from the action of phosphate of soda upon the chloride of calcium is represented by $PO^5, 2CaO + 5HO$.—*Comptes Rendus*, xxvi. p. 205.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a new Process of engraving upon Silver, silvered or gilt Copper, invented by M. Poitevin. *By* M. Becquerel.

M. Niepce de St. Victor has discovered a very ingenious method of copying drawings and engravings upon paper, glass or plates of metal*. M. Poitevin has converted these copies into plates engraved in relief and *intaglio*, after the manner of copperplate engraving, so that any number of proofs may be taken of them. Two or three hours suffice for the operation.

The engraving or manuscript to be copied is first exposed to vapour of iodine, which is deposited solely upon the black portions; the iodized engraving is then pressed gently upon a plate of silver or silvered copper, polished in the same way as for Daguerreotypes. The black parts of the engraving, which have received the iodine, transfer it to the silver, the corresponding parts of which are converted into iodide. The plate, connected with the negative pole of a battery consisting of a few pairs, is then immersed for some minutes in a saturated solution of sulphate of copper, which is connected with the positive pole by means of a strip of platinum. The copper is deposited only on those parts which are not covered with iodide, and which consequently correspond to the white portions. We thus obtain a perfect representation of the engraving, in which the copper represents the white and the iodized silver the black parts. The plate must only remain a very short time in the bath of sulphate of copper; for if the operation were continued too long, the entire plate would become coated with copper.

The plate, after having received the deposit of copper, is very carefully washed, and then immersed in a solution of hyposulphite of soda, to dissolve the iodide of silver which occupies the place of the black parts; it is then washed with a large quantity of distilled water and dried. The plate is then heated sufficiently to oxidize the surface of the copper, which successively assumes different tints; when it exhibits that of a dark brown, it is allowed to cool; the silver exposed is amalgamated, heating the plate gently in order to

* This very interesting process is described at length in the Philosophical Magazine for March 1848.

facilitate the operation. As the mercury does not combine with the oxide of copper, we obtain an impression in which the amalgamated portions represent the blacks, and the parts of the plate covered by oxide of copper the whites; when the amalgamation is finished, the plate is covered with two or three layers of gold leaf, and the mercury evaporated by heat; the gold consequently adheres solely at the places occupied by the blacks of the engraving. The gold which does not adhere is removed with a brush, which being done, the oxide of copper is dissolved in a solution of nitrate of silver, and the silver, as well as the copper which is beneath it, eaten away with dilute nitric acid. The lines of the drawing which are protected by the gold not being attacked, etchings of any depth, corresponding to the white parts of the engraving, may be obtained. When this last operation is done, the plate, which may be compared to an etched copperplate, is fit for taking proofs after the manner of wood-engravings.

To obtain plates engraved after the manner of copperplates, it is requisite to operate on a gilt plate of copper. In the bath of sulphate of copper, the parts corresponding to the whites are again covered with copper; the iodine, or the iodine compound which was formed, is removed with hyposulphite; the layer of deposited copper oxidized; the gold amalgamated, which may then be removed with nitric acid, and at the same time the oxide of copper dissolved. In this way the white parts are evidently preserved, and the hollows represent the black portions, as in engraved copperplates.—*Comptes Rendus*, xxvi. p. 153.

On the Applications of one of the Products of Distillation of Rosin. *By* M. Louyet.

When ordinary rosin (the resin of *Pinus maritima*) is submitted to destructive distillation in an iron retort, two principal products pass over, a yellow essential oil and a very consistent fatty oil. The essential oil, commonly termed *vive essence* by the manufacturers, is a very fluid pyroelaine, of a yellow colour and a very penetrating odour. It contains water, acetic acid and pitch. Hitherto this substance has received no application; and in the manufactories of oil of resin it is regarded as an accessory product of no importance. In making some researches to solve the problem, which has hitherto been considered insoluble, viz. the application of the fatty oil of rosin for the purposes of illumination, and its substitution for the oils derived from the oleaginous grains, I found that the essential oil, or *vive essence*, when suitably rectified over caustic lime, to free it from the acetic acid, water and pitch which it contains, is perfectly well-adapted for the illumination of apartments by burning it in suitable apparatus, for instance in the lamps known in England by the name of Vesta lamps, in which rectified turpentine, commonly known by the name of camphine, is consumed. I have found that the rectified essential oil of the resin, substituted for the pure turpentine in the Vesta lamp, equalled, if it did not excel, the latter.

I also found that it could be used as a perfect substitute for the essential oil of turpentine in all its applications to painting; when mixed with oil colours, it acts as a powerful siccative. I may observe, in conclusion, that the production of this *vive essence* might be considerably increased, should it become an object of demand, by letting the melted resin fall into a vessel filled with coke heated to a dull red.— *Comptes Rendus*, xxiv. p. 183.

On a new Process for bronzing different Metals.

M. Becquerel, at the request of MM. Brunel, Bisson and Gaugain, presented to the Academy pieces of different metals bronzed by an electro-chemical process, which had been applied to the arts.

M. de Ruolz, in 1841, communicated to the Academy a process, by means of which he bronzed some metals, that is to say, he deposited upon them, by means of the battery, coatings of brass or bronze of greater or less thickness. This process, which necessitated the employment of double alkaline cyanides of copper and zinc, or copper and tin, was not adopted in practice, by reason either of the high price of the cyanides, or from other causes.

MM. Brunel, Bisson and Gaugain, instead of the cyanides, employ a solution in water, composed of—

500 parts of carbonate of potash.
20 parts of chloride of copper.
40 parts of sulphate of zinc.
250 parts of nitrate of ammonia.

In order to obtain bronze, a salt of tin is substituted for the sulphate of zinc.

By means of these solutions, wrought or cast iron, steel, lead, zinc, tin, and the alloys of those metals, either with each other or with bismuth and antimony, may with facility be coated with brass or bronze, after being scoured in a suitable manner, according to the nature of the metal. The operation is performed at the ordinary temperature. The article to be coated is put in communication with the negative pole of a Bunsen battery, the positive decomposing pole being a plate of brass or bronze.

When large surfaces are to be coated, experience has proved that it is requisite to increase the number of pairs of plates, and not their size.

When the articles have been coated, and have undergone the usual colouring process, they equal in beauty the finest bronzes.

Rough cast iron may, by these means, be made to assume a very beautiful appearance; and articles thus coated will be preserved from oxidation in the interior of habitations. With regard to those intended for the open air, they must be covered with a suitable varnish, in order to protect them.

"This new process," says M. Becquerel, "of which I have endeavoured to give an idea to the Academy, and which appears capable of rendering great service to the industrial arts, deserves encouragement."—Newton's *Journal*, May 1848.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Influence of Time upon the Formation of Chemical Compounds. *By* Prof. J. LIEBIG.

WHEN effloresced oxalic acid is mixed with an equal weight of alcohol, this liquid takes up a certain quantity of it, far more at a high than at the ordinary temperature. When the alcohol is saturated hot with it, a portion of the oxalic acid again separates on the cooling of the liquid. These facts are so well known, that they would scarcely deserve special mention, did not this solution gradually lose the above properties. In fact, when a boiling saturated solution of oxalic acid in alcohol, which consequently on cooling deposits a large amount of crystals, is kept for some time at a temperature of 104° to 122°, the quantity of the crystals deposited on cooling decreases after some days, and in the course of several months this liquid no longer affords any crystals. Long before this time a considerable amount of oxalovinic acid and oxalic æther may be detected in the solution; and at last so much of the latter, that on the addition of water it separates in the usual heavy oily drops. On saturating the liquid with chalk, a quantity of lime remains in solution as oxalovinate; on mixing it with ammonia, a considerable quantity of oxamide is obtained. Hippuric acid behaves in exactly the same manner. From a hot saturated alcoholic solution this acid crystallizes in the well-known long needles; but if the solution be kept for several weeks in a warm place, the form of the deposited crystals varies perceptibly, the needles become shorter and shorter, and the acid subsequently separates in cauliflower-like masses, without any distinct form. At last crystals are formed, which melt like an oil at a gentle heat, and possess all the properties of hippuric æther.

It is not every acid however that is converted into an æther by contact with alcohol under similar circumstances; benzoic acid may be kept for weeks in a warm spot with alcohol, without the crystals which separate on cooling being altered in form or in size; but if a hot saturated alcoholic solution of this acid, which on cooling would solidify to a solid paste, is mixed with a few drops of fuming hydrochloric acid, or, which is preferable, with some alcohol which has been saturated with hydrochloric gas, and the mixture kept at a gentle heat from eight to fourteen days, it entirely loses the pro-

perty of depositing crystals on cooling. The greater portion of the benzoic acid is converted into benzoic æther, which, on the addition of water and carbonate of soda to remove the hydrochloric and free benzoic acids, separates on the application of a gentle heat in transparent oily drops, which collect at the bottom on cooling. This behaviour of the hydrochloric acid appears to me deserving of consideration, as the action of the very minute quantity present appears to resemble that of the deutoxide of nitrogen in the formation of sulphuric acid. It is known that the chloride of benzoyle mixed with alcohol is instantly metamorphosed into hydrochloric acid and benzoic æther; and it is not impossible that the hitherto enigmatic part which this hydracid takes in the formation of several æthers depends on the production of chlorine compounds, by the decomposition of which with alcohol the hydrochloric acid is constantly set free again, so that a minute quantity suffices to convert an unlimited amount of acid into æther. I do not, however, mean to deny that this reaction admits of other modes of explanation.

The formation of acetic æther and of œnanthic æther in wines on keeping, appears to take place in a very similar manner. It is well known that wines possessing a considerable bouquet, when submitted to distillation, yield a residue of a very disagreeable taste and a distillate containing much alcohol; and that, on mixing the two, a liquid is obtained which has not the least resemblance in taste to the original wine. Geiger observed, that when the distillate mixed with the residue was kept for several years in a cool spot, the original wine was reproduced with scarcely any perceptible difference in taste and odour. It appears, according to this, that what is termed the "bouquet" of wine is owing to the formation of æther compounds; and we may expect that, by a careful examination, their nature will be ascertained; it is not at all doubtful that they can be prepared artificially.—Liebig's *Annalen* for March 1848.

On some Products of Decomposition of Chrysammic Acid. *By* E. Schunck, *with Remarks by* Ch. Gerhardt.

According to some recent experiments, published by Mr. Schunck in Liebig's 'Annalen' for February of this year, chrysolepic acid is identical with nitropicric acid, as previously asserted by several chemists. Aloe-resinic acid, previously described by the same chemist, is produced by the action of potash upon chrysammic acid, and is not obtained, as formerly stated by Mr. Schunck, directly from aloes and nitric acid.

Aloetic acid, treated with concentrated nitric acid, is wholly converted into chrysammic acid; nitrous acid is given off, but no other collateral product is formed than oxalic or nitropicric acid. On the other hand, chrysammic acid experiences no change on treatment with fuming nitric acid. Aloetic acid furnished on analysis,—carbon, 40·75; hydrogen, 1·73; nitrogen, 11·59; from which the author deduces the relations $C^{16}\,H^{4}\,N^{2}\,O^{13}$, which do not appear to me to be accurate. When chrysammic acid is boiled with ammonia, it dis-

solves to a dark purple liquid, which on cooling deposits needles of a reddish-brown colour by transmitted, and metallic-green by reflected light. Mr. Schunck found it to contain 37·61–37·88 carbon, 2·35–2·21 hydrogen, and 19·72–19·87 nitrogen. He calls it chrysamminamide; but this product is evidently identical with the chrysammide of M. Mulder.

If dilute sulphuric or hydrochloric acid is added to a boiling solution of chrysammide, dark needles separate on cooling, which when dry are of a dark olive-green colour. This substance is a true acid, which is called amidochrysammic acid; it was found to contain 38·65–38·77 per cent. C, 1·85–1·92 H, and 18·24–18·29 N.

Mr. Schunck is of opinion that the formulæ $C^{14} H^4 N^3 O^{11}$ and $C^{15} H^4 N^3 O^{12}$ both agree sufficiently well with experiment, and that as yet the preference cannot be assigned to either; but if we take into consideration the recent analyses of chrysammic acid of Prof. Mulder, it is evident that the formula C^{15} cannot be admitted. The baryta salt of this acid was obtained by dissolving the acid in ammonia and adding chloride of barium, in the form of a red crystalline precipitate, which yielded on analysis 29·93 carbon, 1·77 hydrogen, and 25·11 per cent. sulphate of baryta. Concentrated boiling acids, especially nitric and sulphuric acids, convert the amido-chrysammic acid again into chrysammic acid*. The salts detonate when heated like the chrysammates; they present nearly the same appearance as the latter, but are easily distinguished by their liberating ammonia when treated with potash; they are obtained by double decomposition. When chloride of barium is added to an aqueous solution of chrysammide, no precipitate takes place in the cold; but on ebullition a dark red crystalline powder separates, which consists of amido-chrysammate of baryta. The solution at the same time contains chloride of ammonium; but the precipitation of the amido-chrysammate of baryta is instantaneous when ammonia is added to the mixture of chrysammide and chloride of barium†. When chrysammic acid is boiled with an excess of caustic potash, it dissolves to a brown solution, which yields a brown precipitate on the addition of acids. It is soluble in pure water. Mr. Schunck states that this body is identical with his aloe-resinic acid.

When chrysammic acid is boiled with potash, and chloride of barium subsequently added, a salt is obtained which contains 28·03 carbon, 1·82 hydrogen, and 30·80 baryta, numbers which lead to the formula $C^{12} H^4 N^2 O^{7} BaO$. Starting from the formula recently assigned by Mulder to chrysammic acid, we have

$$C^{14} H^2 N^2 O^{12} + 2HO = 2CO^2 + C^{12} H^4 N^2 O^{10};$$

whence it is seen that 2 equivalents of carbon of the chrysammic acid have remained in combination with the potash in a state of

* The name of this acid is evidently ill-chosen; it should be replaced by that of chrysic acid, and the name of chrysammic acid reserved for the amidogen acid. —C. G.

† Prof. Mulder, in his analysis of chrysammine prepared in the moist way, found nearly the same numbers as those obtained by Mr. Schunck in the analysis of his amido-chrysammic acid. The two bodies are evidently identical.—C. G.

carbonate. Mr. Schunck, who interprets the reaction by the following equation,—

$$C^{15}H^{2}N^{2}O^{13} - 3CO^{2} + 3HO = C^{12}H^{5}N^{2}O^{10},$$

supports himself by a formula which is evidently incorrect. It should also be observed, that the formula $C^{12}H^{4}N^{2}O^{10}$ renders aloe-resinic acid isomeric with M. Laurent's nitrophenesic acid.

When chrysammic acid is added to a boiling solution of sulphuret of potassium containing an excess of caustic potash, it dissolves with a beautiful blue colour; on cooling, the solution deposits beautiful needles, which appear blue by transmitted, and red with a metallic lustre by reflected light. This new substance is called hydrochrysammide. To purify it, it is dissolved in boiling potash, from which it separates in the crystalline state. Although formed in an alkaline solution, it contains no potash, and is perfectly neutral. When heated in a test-tube, it gives off violet vapours, which condense in the cold portions to blue crystals; but the greater part is decomposed with disengagement of ammonia, leaving a considerable carbonaceous residue. It is insoluble in boiling water, slightly soluble in boiling alcohol, to which it imparts a faint blue colour. It dissolves in concentrated sulphuric acid with a brown colour, and is again precipitated by water in blue flakes. Boiling nitric acid decomposes it; it is likewise gradually decomposed and dissolved when suspended in water, and chlorine is passed through it. It dissolves in potash and in the carbonated alkalies; the solutions possess the same colour as sulphindigotic acid and its compounds; acids precipitate it from these solutions in blue flakes. It contains no sulphur, nor is it necessary to employ sulphuret of potassium in its preparation; for if chrysammic acid is added to a boiling solution of protochloride of tin, it instantly turns blue; and after removing the excess of acid, and dissolving the residue in boiling caustic potash, hydrochrysammide separates on cooling; but it is difficult by this method to obtain it perfectly free from oxide of tin. On analysis it afforded 50·77–50·51 per cent. of carbon, 3·48–3·57 hydrogen, and 15·36–15·28 nitrogen, numbers which lead to the formula $C^{14}H^{6}N^{2}O^{6}$. —*Journ. de Pharm.*, April 1848.

On the Essential Oil of Matricaria Parthenium.
By Messrs. Dessaignes *and* Chautard.

The plant was collected during the period of flowering, and the upper half, stem, leaves and flowers submitted to distillation; a small quantity of a greenish volatile oil was collected. The oil obtained in the dry hot summer of 1846 became filled in the course of twenty-four hours with large crystalline laminæ of stearoptene. No trace of stearoptene was obtained from oil distilled in 1845. The produce of the two years was united, and exposed to a temperature of 24° F., when it deposited numerous crystals. The stearoptene separated from the oil was strongly pressed between folds of paper, and then exposed to the air for several days. The mass,

at first homogeneous and granulated, when thus deprived of oil became firm, brittle, and assumed a crystalline appearance. The pure stearoptene has a strong odour of camphor; it melts at 347°, boils at 399°. The stearoptene, when burned with oxide of copper, gave—

	Found.	Calculated.
Carbon	78·76	78·94
Hydrogen	10·69	10·53
Oxygen	..	10·53

It is consequently identical with the camphor of the laurels, the presence of which has already been pointed out by Proust in several volatile oils derived from the *Labiatæ*, and which is now shown to exist in a plant belonging to the *Compositæ*. The oil of *Matricaria*, separated from the camphor by the preceding operations, dried over chloride of calcium, and burnt, furnished carbon, 77·60, and hydrogen, 10·37. Some oil prepared in 1847, and which had spontaneously deposited a small quantity of camphor, was dried over chloride of calcium and analysed; it gave 77·96 per cent. C, and 10·60 H.

The oil of *Matricaria* is evidently a mixture; even that which has been submitted to great cold still contains a considerable quantity of camphor. It began to boil at about 310°, but the thermometer rose rapidly to 400°, and the greater portion of the oil distilled over between 400° and 428°, leaving a coloured residue. The last half of the product, which had been collected between 394° and 428°, deposited, when submitted to a very low temperature, a large amount of camphor, which was separated. The oil was distilled several times over caustic lime, collecting the products at separate intervals; but no oil was obtained with a constant boiling-point. All the portions collected between 392° and 428° always afforded camphor on cooling, and sometimes to such an extent that the product of distillation congealed to a soft mass in the neck of the retort. We will enumerate a few of our analyses. I. is of oil collected between 310° and 334°; II. between 338° and 356°; III. between 390° and 420°; and IV. between 420° and 428°:—

	I.	II.	III.	IV.
Carbon	86·46	85·77	77·02	76·92
Hydrogen	11·58	11·22	10·24	10·37

The volatile oil of *Matricaria* most probably contains, besides camphor, a hydrocarbon of the formula $C^5 H^3$, and an oil containing more oxygen than camphor.—*Journ. de Pharm. et de Chim.*, April, p. 241.

On the Presence of Copper and some other Metals in the Blood and Liver of Man and the lower Animals. By MM. MILLON, DESCHAMPS *and* HARLESS.

M. Millon ascertains the presence of different metals in the blood by a very simple mode of analysis. The blood, as it escapes from the vein, is received in about three times its bulk of water, and the fluid poured into a bottle of chlorine and agitated. It immediately

coagulates, becomes brown, and finally gray, and the fluid part is rapidly and easily filtered off. In the filtered fluid he readily determined the presence of copper, lead, manganese and silica. He further ascertained that the copper and lead are, like irón, attached to the globules, and not distributed through the mass of the blood. A kilogramme of the clot having given 0·083 grm. of those metals, while the same weight of serum gave only 0·003, a quantity no doubt due to the solution or suspension of a minute proportion of globules in the serum. It is probable, from the facts thus ascertained, that these metals, like iron in the blood, participate in some physiological function, which however it is impossible for us at present to define. —*Académie des Sciences*, Jan. 10, 1848.

M. Deschamps, on his part, has endeavoured to trace the source of what he calls the physiological copper; and he concludes from his investigations, that all soils contain copper, derived in all probability from the decomposition of copper pyrites; that vegetables extract a portion of the copper from the soil, which afterwards finds its way into the animal system along with the food, though in the case of man a certain portion of copper and lead may obviously be derived from the vessels in which his food is cooked. The copper appears to be contained in the soil as carbonate; and as that salt is soluble in carbonate of ammonia, M. Deschamps considers it to be the substance by the assistance of which the copper is carried into the vegetable system, in which it is permanently deposited by the decomposition of the ammonia, for the formation of the nitrogenous constituents of the plant.—*Académie des Sciences*, Jan. 1848.

Harless has made a variety of very important observations on the blood of the Ascidia and of the Cephalopoda generally. He had observed that, in these animals, the blood, although perfectly colourless in the vessels, becomes deep blue when permitted to escape. The production of this blue colour he found to depend solely on the carbonic acid of the air. When a single bubble of that gas is sent through the blood, the blue colour is produced, and gradually becomes darker as the current of the gas continues; but it is again almost, though not altogether, deprived of its colour by agitation with oxygen. The blood of *Eledone* presented these phænomena after being carried from Trieste to Nurnberg. Analysis of the blood by Von Bibra gave the following results:—

Water	92·67
Solids	7·33
	100·00

100 parts of the dry blood gave of ash 35·88.
100 parts of the ash consisted of—

Chloride of sodium	73·1
Sulphate of soda	2·0
Phosphate of soda, a doubtful trace	24·9
Phosphate of lime and copper	
	100·0

Iron was entirely absent, and appears to have been replaced, both here and in the liver, by copper. He found in the ash of the liver 1·12 per cent. of copper, the presence of which was fully determined by a little galvanic circuit of zinc and platinum, by sulphuretted hydrogen, and by the blowpipe. The presence of copper in the liver reminds us of its discovery in certain biliary calculi by Bertozzi, Heller and Gorup-Besanez; but its constant occurrence, and its replacing the iron of the blood, sufficiently show that the opinion put forth by those chemists, of the liver being the organ through which foreign metals are thrown off from the system, is inadmissible. As regards the source of the copper, Harless considers it impossible that it could be derived from the sheathing of ships, as those animals in which he detected it were caught at a distance from harbours in which such vessels lie; and he concludes that it must have been taken in along with their food, which in the Cephalopoda consists of Crustacea and small fishes. He has found copper in the *Cancer pagurus*, *Acanthias zeus* and *Conger vulgaris*, and in quantities always inversely proportional to the iron which they contain.

The blood of the *Helix pomatia* likewise contains a large quantity of copper, that portion of the ash which was insoluble in water having given 2·57 per cent. of metallic copper. This blood, at least in winter, becomes blue by exposure to the air; but, what is very remarkable, under totally different circumstances from those which produce the coloration in the *Eledone*, the blue being destroyed by carbonic acid and restored by oxygen, an experiment which could be repeated many times on the same blood. In the blood of the *Helix pomatia*, alcohol produces a colourless coagulum. Ammonia destroys and hydrochloric acid restores the blue colour. The colouring matter is precipitated by alum, and rapidly dissolved by an excess of the precipitant; but by the addition of ammonia it is entirely thrown down. The compound of alumina and the colouring matter gave 29·53 per cent. of a green ash containing a large quantity of copper.—Muller's *Archiv*, No. 2, 1847; and *Edinburgh Monthly Journal*, May 1848.

On the Nitrate of Amylene. *By* W. Hofmann.

The author has succeeded in obtaining this product by acting with nitric acid on potato fusel oil in the presence of a large amount of nitrate of urea. The nitrate of amylene is a colourless liquid, of a disagreeable odour, resembling that of bugs; it is scarcely soluble in water, and boils at 298° F. An alcoholic solution of potash decomposes it, amylic alcohol and crystals of nitre being formed; its formula is $C^{10} H^{11} O, NO^5$.—*Comptes Rendus*, xxvi. p. 184.

On the Neutral Salts of Uric Acid. *By* J. Allen *and* A. Bensch.

A few years ago Dr. Bensch made us acquainted with the neutral anhydrous combinations of uric acid with potash and soda*. In the

* Chem. Gaz., vol. iii. pp. 413, 426.

following communication several other neutral salts of uric acid are described.

Neutral Urate of Potash, KO, $C^5 N^2 HO^2$, is obtained by dissolving uric acid diffused in water in cold dilute caustic potash (perfectly free from carbonate) until the latter dissolves nothing further; the solution is then concentrated in a retort. At a certain degree of concentration the salt separates in crystals from the boiling solution. It is washed first with weak, and subsequently with strong alcohol. The salt thus prepared is easily soluble in water, has a very caustic taste, rapidly absorbs carbonic acid from the atmosphere, and is quickly decomposed on ebullition with water. The crystals are anhydrous, for when first dried at the ordinary temperature in a current of hydrogen, they lost no more in weight at 248°. At 302° the salt turns yellow, and at a higher temperature black; it then melts, and is very difficult to burn white. Dried in a current of hydrogen at 248°, it afforded on analysis—

Carbon	24·24	24·20	5 =	24·49
Hydrogen	0·96	0·92	1	0·82
Nitrogen	..	..	2	23·12
Oxygen	..	..	2	13·05
Potash	38·18	38·25	1	38·52

Neutral Urate of Soda, NaO, $C^5 N^2 HO^2$ + HO (at 212°), is obtained in the same manner as the potash salt. It separates, on the cooling of the concentrated ley, in hard warty crystals, which are first rinsed with water, and afterwards with weak spirit. The salt, dried at 212°, gave 27·34 per cent. of soda, which corresponds to the above formula. Both this and the preceding salt appear to be decomposed by water.

Urate of Ammonia.—The neutral salt does not appear to exist. On mixing the neutral salt of potash with acetate or muriate of ammonia, as well as on treating uric acid with an alcoholic solution of ammonia, the salts obtained always contained 1 atom of ammonia to 2 of acid.

Urate of Magnesia does not appear to exist in the neutral state, nor could neutral double salts of the urate of magnesia with potash, soda and ammonia be prepared. When a boiling solution of a salt of magnesia is mixed with a dilute solution of the neutral urate of potash, a gelatinous precipitate separates, which is partly soluble in hot water, biurate of magnesia can be extracted from it, and the residue consists of hydrate of magnesia. If the boiling solution is filtered quickly, the entire liquid solidifies to a stiff, perfectly clear jelly, which after a time becomes turbid; it liquefies on the application of heat, and on long-continued ebullition deposits hydrate of magnesia. From this behaviour the existence of a neutral salt of magnesia might be concluded; but a precipitate is obtained on the addition of alcohol to the gelatinizing liquid, which is an acid salt; for when dried at 212°, it contained 7·6 per cent. magnesia and 67·7 anhydrous uric acid. On the examination of the precipitate formed on boiling a solution of magnesia with neutral urate of potash, the

former in excess, it was always found to contain several per cent. of potash. It contains 1 equiv. uric acid to 1 equiv. magnesia; but since it constantly leaves a residue of magnesia on solution, it may be equally admitted that a mixture of hydrate of magnesia with acid salt falls; otherwise the preparation of the neutral salt by boiling uric acid with hydrate of magnesia should succeed. Moreover, it was found that the longer the liquid was boiled, the more magnesia the precipitate contained, which amounted even to 26 per cent.

The neutral salts of uric acid with the alkaline earths are easily obtained by boiling solutions of the pure bases with uric acid, or by decomposing a salt of the earth with neutral urate of potash; in the latter case the solution of the neutral urate of potash is first boiled with a small quantity of the salt, when carbonate is first precipitated, and then the pure salt.

The Neutral Urate of Lime, $CaO, C^5 N^2 HO^2$ (at 212°), is obtained, by the method above described, on boiling the solution of neutral urate of potash to which chloride of calcium is gradually added for an hour, when the salt separates in hard heavy granules; it is likewise obtained on mixing lime-water with uric acid. The salt does not appear to be crystalline under the microscope; it gave on analysis—

Carbon	27·09	..	5	29·13
Hydrogen	..	..	1	0·97
Nitrogen	1·47	..	2	27·19
Oxygen	..	..	2	15·53
Lime	27·34	27·03	1	27·18

Neutral Urate of Strontia, $SrO, C^5 N^2 HO^2 + 2HO$ (at 212°).—This salt is obtained by dissolving uric acid in boiling strontian water; it is soluble in water, has an alkaline reaction, and parts with its water at 329°. The salt, dried at 212°, gave on analysis—

Strontia	36·37	36·32	1	= 35·78
Uric acid	49·85	..	1	51·73
Water	11·13	..	1	12·49

Neutral Urate of Baryta, $BaO, C^5 N^2 HO^2 + HO$, prepared in the same manner, contained when dried at 212°, 47·84 baryta, 46·47 uric acid, and 5·69 water; dried at 338°, it afforded 39·12 baryta, 20·64 carbon, and 0·84 hydrogen; these last numbers correspond to the formula $BaO, C^5 N^2 HO^2$.

Neutral Urate of Lead, $PbO, C^5 N^2 HO^2$ (at 212°).—A dilute solution of neutral urate of potash is added by drops to an equally dilute solution of nitrate of lead; the yellow precipitate which at first subsides is rejected; subsequently a perfectly white lead salt is deposited, which is amorphous, and can be heated up to 320° without decomposition. It afforded on analysis 58·76 oxide of lead, 13·91 carbon, and 1·09 hydrogen. When heated up to 302°, but a very small quantity of water was given off; it appears therefore that the salt is rendered anhydrous at 212°.

It was found impossible to prepare the neutral salts of uric acid with the oxides of the heavy metals.

The authors give the following tabular arrangement of the solubility in water of some of the urates, which may prove important in a physiological or pathological point of view:—

	Water.	
	Cold.	Boiling.
1 part Neutral urate of potash requires for solution	44	35
Biurate of potash	790	75
Neutral urate of soda	77	85
Biurate of soda	1150	122
Biurate of ammonia	1600	undeterm.
Neutral urate of baryta	7900	2700
Biurate of baryta	insol.	insol.
Neutral urate of strontia	4300	1790
Biurate of strontia	5300	2300
Neutral urate of lime	1500	1440
Biurate of lime	603	276
Biurate of magnesia	3750	160

Liebig's *Annalen*, lxv. p. 184.

On the Composition of Quinone. By Prof. Wöhler.

Woskresensky calculated from the results of his analysis of quinone the relative composition C^3 HO for this body; according to an analysis which I made of quinone, probably modified by melting, I obtained a higher amount of carbon, and considered myself compelled to adopt for this body the formula C^{25} H^8 O^8, in accordance with its metamorphoses. In the 'Comptes Rendus' of 1845 M. Laurent has stated, that, according to his analysis, quinone contains only 24 atoms of carbon. Dr. Städler has, at my request, tested this assertion, and has proved it to be perfectly correct by two analyses. Quinone has therefore the original per-centage composition found by Woskresensky, and is C^{24} H^8 O^8, with which the numbers found by myself for the composition of all its products of metamorphosis agree much better than with the formula I previously adopted.—Liebig's *Annalen* for March 1848.

On the Spontaneous Combustion of the Residue from the Preparation of Acetone. By M. Pfeffer.

Krafft of Moscow observed, in preparing some acetone, that the residue underwent spontaneous combustion by exposure to the air. I have recently had occasion to confirm this statement. Although Prof. Hünefeld made known, as far back as 1837, that the acetate of lead heated to redness burnt in contact with the air, the observation of M. Krafft nevertheless deserves being published, in order to prevent accidents, which might result from this combustion.—*Journ. de Pharm.*, May 1848.

ANALYTICAL CHEMISTRY.

On the Estimation of Urea. *By* Prof. R. Bunsen.

Aqueous solutions of urea are very readily decomposed into carbonate of ammonia, when heated above 212°, in hermetically closed vessels. The metamorphosis begins even below 248°, but proceeds so slowly at this temperature that it is not completed in three or four hours; while if the temperature is kept between 428° and 464°, three or four hours suffice for perfect decomposition. This reaction affords a ready means of determining the amount of urea in liquids, for it suffices to heat them with an ammoniacal solution of chloride of barium up to 428°–464°, to obtain a precipitate of carbonate of baryta equivalent to the amount of urea.

The following experiments show the degree of accuracy which may be attained by this method. They were made with urea, prepared from urine and likewise from cyanate of ammonia, which, with the perfectly clear ammoniacal solution of chloride of barium, was inclosed in strong glass tubes, and then exposed for three hours, at a temperature of 400°–464°, in an oil-bath :—

I.	0·1458 grm.	urea gave	0·4771 carbonate of baryta.
II.	0·1884	...	0·6183 $BaCO^2$.
III.	0·2938	...	0·9633 $BaCO^2$.

Consequently out of 3 parts urea, a quantity corresponding to the average amount in 100 parts of urine, there were obtained by experiment—

I.	II.	III.
2·986	2·994	2·991

This agreement may be looked upon as satisfactory; but the practical value of such determinations depends also on another circumstance, viz. the acquired certainty that the different nitrogenous substances present in the urine do not, at the same time with the urea, produce carbonate of ammonia when heated. Hippuric and benzoic acids gave rise to no turbidness on treatment with an ammoniacal solution of chloride of barium at a high temperature, and are consequently not subject to any such decomposition. Uric acid experiences a metamorphosis like urea under similar circumstances, carbonate of ammonia being one of the products; but even boiling saturated solutions of a urate are so completely precipitated on cooling by chloride of barium in the presence of ammonia, that the presence of this acid, however considerable its amount, cannot interfere with the results, if the urine under examination is precipitated by an ammoniacal solution of chloride of barium before being heated, and, after removing the precipitate, heated in the oil-bath. To obtain perfect certainty on this subject, a saturated solution of urate of ammonia was precipitated with an excess of ammoniacal solution of chloride of barium, set aside for some time, and after removing the copious precipitate, used to decompose various amounts of urea.

Of 3 parts of urea employed, the author obtained in three experiments—

2·948 2·966 2·921

To decide the question, whether the presence of readily decomposable animal substances deteriorates the accuracy of the method, an aqueous extract of a mixture of milk, white of egg, coagulated blood, muscular fibre, tendons, nasal secretion, fat, saliva, diabetic sugar, chloride of sodium, sulphate of soda and phosphate of ammonia was used as solvent for the urea to be determined, after the precipitate produced by the alkaline solution of chloride of barium had been separated from the liquid, which passed clear through the filter. In four experiments the author obtained of the 3 parts employed—

2·932 2·980 2·934 2·961

When mixed with the above-mentioned animal substances, but in a different proportion, and with an admixture of gelatine and a few drops of bile instead of diabetic sugar, the author obtained for 3 parts of urea employed—

2·879 2·961 2·985

It is evident therefore that these determinations, even in the presence of substances the most widely diffused in the animal body, possess a sufficient degree of accuracy. Solutions of such substances become, it is true, when heated with an ammoniacal solution of chloride of barium up to 464°–480, very slightly turbid from the deposition of an empyreumatic substance, the quantity of which however is so inconsiderable, that, compared with the weight of the carbonate of baryta, it cannot be taken into consideration. It is owing to this that the separated baryta salt usually exhibits a faint yellowish tint, and cannot be obtained perfectly white after ignition in a closed crucible. The form in which the carbonate of baryta separates in this decomposition is very remarkable. It forms regular acicular crystals, frequently a line in length; this is not owing, as might at first be supposed, to a slow elimination of the salt proceeding simultaneously with the decomposition of the urea, but rather to its solubility in a solution of chloride of ammonium at a high temperature. From this circumstance it may be conjectured that the carbonates of baryta, strontia, oxide of lead, &c. dissolve under similar circumstances, and again separate in crystals on cooling.

The most important question, the solution of which must principally decide as to the value of this mode of determination, regards the influence which the so-called extractive substances of the urine exert. I at first strongly doubted as to the solution of this problem. The substances comprised under the common name of extractive substances cannot be separated without at the same time experiencing a change, of which it is uncertain whether it be connected with an elimination of carbonate of ammonia or not. It is impossible to submit these mutable substances alone to such a test, and in the form in which they are contained in the urine; it is just as impossible to remove the urea by any method which would exclude

the possibility of a simultaneous alteration of the other constituents; one plan then only is left, that is to determine the urea from two portions, one of which has been previously deprived of its extractive substances by basic acetate of lead, in order from the agreement of the two results to arrive at a conclusion as to the behaviour of these substances towards the solution of the chloride of barium employed for the decomposition. For such an experiment to be decisive, all influences must be avoided which might produce any metamorphosis of the urea or of those substances. This condition may be satisfied in the following manner:—

A weighed quantity of urine, A, is precipitated with a weighed quantity of an ammoniacal solution of chloride of barium, B. From C parts by weight of this liquid, filtered from the precipitate and carefully preserved from evaporation, which have been weighed in a strong glass tube containing some solid chloride of barium, and then hermetically sealed, the per-centage amount of urea of the original urine may readily be calculated, if the weight of the first baryta precipitate, b, and that of the carbonate of baryta, k, formed on heating, have been determined.

The weight of the material A employed becomes on the addition of chloride of barium $A + B$; this is composed of the weight of the precipitate b and of that of the liquid containing the urea. The whole of the urea originally contained in A is consequently now contained in the liquid precipitated by chloride of barium, $A + B - b$. Now if in C parts by weight of this liquid, $A + B - b$, an amount of urea f is found, the quantity of urea contained in the original amount of urine A is $\frac{f(A+B-b)}{C}$, whence the per-centage amount of urea in the urine is $\frac{100 f (A+B-b)}{AC}$.

In this expression there is now only the quantity f to determine. Since 1 atom of urea gives 2 atoms of carbonate of baryta, we obtain from the amount of carbonate of baryta, k, found, the corresponding quantity of urea, f, by multiplying k by

$$\frac{C^2 + H^4 + N^2 + O^2}{2\,(Ba + C + O^3)} = 0{\cdot}3041.$$

Hence the per-centage amount of the urea in the urine results from the formula

$$H = \frac{30{\cdot}41\, k\,(A + B - b)}{AC}. \quad . \quad . \quad . \quad . \quad (1.)$$

To perform the same determination after the removal of the extractive substances, another portion of the same urine is precipitated with ammoniacal solution of acetate of lead, and the precipitate separated from the liquid, carefully avoiding any loss by evaporation. A portion of this filtered liquid is freed from lead by a clear solution of chloride of barium in dilute sulphuret of ammonium. After removing the sulphuret of lead, a portion of the liquid containing the sulphuret of ammonium, and carefully protected from evaporation, is decomposed with chloride of barium at 428°–464°,

and the carbonate of baryta eliminated determined. Lastly, the two lead precipitates have to be collected on weighed filters, and after washing, dried and weighed.

If A′ represent the weight of the urine employed, B′ that of the solution of the acetate of lead, and b' that of the lead precipitate produced, the same amount of urea is contained in the liquid A′ + B′ − b' as in A′. If C′ parts of this liquid A′ + B′ − b' be employed, they must contain as much urea as was contained in $\frac{A' C'}{(A' + B' - b')}$ parts of the original urine, because

$$(A' + B' - b') : C' :: A' : \frac{A' C'}{(A' + B' - b')}.$$

If to this solution C′ the weight D of sulphuret of ammonium is added, and the amount d of sulphuret of lead separates, the liquid C′ + D − d contains the same quantity of urea as was contained in $\frac{A' C'}{(A' + B' - b')}$ parts of the original urine. If, lastly, the quantity E of this amount of liquid C′ + D − d is employed for decomposition with chloride of barium, this quantity E contains as much urea as is contained in $\frac{A' C' E'}{(A' + B' - b')(C' + D d)}$ parts by weight of the original urine, as is evident from simple proportion. If k' parts of carbonate of baryta are obtained from this quantity E by heating with chloride of barium in a closed glass tube, the percentage amount of urea in the urine is found as above by:—

$$H' = \frac{30{\cdot}41\, k' (A' + B' - b')(C' + D - d)}{A' C' E}. \quad . \quad . \quad . \quad . \quad (2.)$$

To decide, by means of these formulæ, the question as to the influence of the extractive substances, two portions of the same urine were examined. The first, in which the amount of urea was ascertained, after getting rid of the extractive substances by means of the formula (2.), gave the following data for calculation:—

Weight of the urea employed	50·5157	= A′
Weight of ammoniacal solution of lead added	128·5680	= B′
Weight of precipitate produced.....	6·1071	= b'
Weight of liquid precipitated with solution of lead employed	56·4128	= C′
Weight of the sulphuret of ammonium containing chloride of barium added	9·3285	= D
Weight of sulphuret of lead precipitated	1·7052	= d
Weight of filtered ammoniacal solution employed	27·3451	= E
Weight of carbonate of baryta obtained	0·5493	= k'

On substituting these values in the equation (2.), the amount of urea contained in the urine is found to be 2·374 per cent.

The second portion of the same urine in which the amount of urea was to be ascertained with the assistance of the formula (1.), without any previous removal of the extractive substances, gave the following data:—

Weight of urine employed	47·7660	= A
Weight of solution of chloride of barium added	68·0050	= B
Weight of baryta precipitate	0·8850	= *b*
Weight of filtered solution employed	18·1410	= C
Weight of carbonate of baryta obtained	0·6068	= *k*

On repeating the experiment with the same liquid from which the baryta precipitate *b* had been separated by filtration, for 19·0785 = C, 0·6397 = *k* were obtained.

On calculation, the two experiments gave 2·446 and 2·452 per cent. of urea, an almost perfect agreement. But the same urine, previously deprived of its extractive substances, afforded, according to the above experiments, 2·374 per cent. From the slight difference between these three determinations, which does not exceed the limits of an error of observation, it may be concluded that the presence of extractive substances has no essential influence in determinations of urea according to this method.

The method of investigation will, after these explanations, be evident.

From 50 to 60 grms of urine are weighed off in a digesting flask, which has been previously dried or rinsed with the liquid under examination, and the margin of which is smeared with a little fat; the greater portion of it is then poured off into another dry digesting flask, and the weight of the decanted quantity A determined by weighing again the partially emptied vessel. The urine, weighed off in this manner, is precipitated by a most concentrated solution of chloride of barium containing some free ammonia, and the weight of the baryta solution added, B, determined in the same manner. As soon as the precipitate has subsided, after agitating the corked flask, the supernatant liquid is poured upon a weighed filter, which has not been previously moistened, and from 25 to 30 grms. of it allowed to flow through a long-necked glass funnel, drawn out to a point, into a strong counterpoised glass tube sealed at one end, which contains about 3 grms. of solid chemically-pure chloride of barium, and the sides of which above the level of the liquid are carefully preserved from becoming moist by the long-necked funnel. After the weight of the introduced liquid, C, has been determined by again weighing the tube, this is sealed before the glass-blower's lamp at from 1 to 1½ inch above the level of the liquid, taking care while drawing out the glass to thicken it sufficiently.

In the meantime the whole of the baryta precipitate is brought upon the weighed filter, washed, and its weight *b* determined. The metamorphosis of the urea in these hermetically-sealed tubes is best effected in a copper oil-bath, heated over a lamp, which is traversed by copper tubes, closed at one end for the reception of the sealed glass tubes. When tubes are made with glass 2·5 millim. thick, the bore of which does not exceed 15 millim., no explosion need be feared at a temperature of 428° to 464°, which moreover would be perfectly free from danger if the apertures of the tubes or the door of the oil-bath were turned from the observer. After being heated from three to four hours, the oil-bath is left to cool; the glass tubes

are cut by passing a file over them, and then separated by means of a piece of incandescent charcoal, in order to collect the eliminated crystals of carbonate of baryta upon a small filter, and, after washing with water free from carbonic acid, to determine their weight, *k*. If, as is usually the case, the crystals adhere at certain spots of the glass, they are easily removed by means of a thick platinum wire, beaten out at one end into a small spatula. On substituting the values of the found weights A, B, C, *b*, *k* in the formula

$$H = \frac{30{\cdot}41\,k\,(A + B - b)}{A\,C},$$

we obtain for H the per-centage amount of urea in the urine.

I will enumerate, as an example, a couple of analyses, for which two portions of one and the same morning urine were employed:—

	I.	II.
A =	26·6795	27·491
B =	8·3820	19·388
b =	0·7227	0·724
C =	18·4305	23·179
k =	1·5933	1·540

Experiment I. gives 3·383 per cent. and II. 3·392 per cent. urea.

The mode of determining the other constituents of the urine requires no explanation. I will only add a few words respecting the small unavoidable error which occurs in these determinations, as in every other analytical method. The first source is owing to the imperfect insolubility of carbonate of baryta in pure water and in water containing chloride of ammonium. A glance at the experiments suffices to show that the error, owing to this cause, is always in the same direction, decreasing the result found. It affects the absolute accuracy of the experiment the more the smaller the quantity of urea contained in the urine under examination. But a glance at the numerous experiments performed, purposely under the most unfavourable circumstances, will show at once that it does not exceed the limit of error admissible in analyses of the urine; it may perhaps be possible to increase this accuracy by employing a salt of lime, instead of one of baryta, for decomposing the urea. At all events, carbonate of lime does not appear to dissolve in a similar manner in chloride of ammonium at a high temperature. Such a modification of the method, however, would be accompanied with other inconveniences, and render the advantages doubtful.

A second unavoidable but equally unimportant source of error is the small amount of creatine contained in the urine. As was to be supposed, this substance is decomposed, when heated with an ammoniacal solution of chloride of barium above 392°, into ammoniochloride of sarcosine and carbonate of baryta. The slight amount of creatine however contained in the liquid barely renders necessary any allusion to this source of error, which moreover compensates for that produced by the solubility of the carbonate of baryta.

Considering that, without any great analytical skill, one person may easily perform in a day and a half eight or ten such determina-

tions of urea, it will scarcely be denied that, of the various methods hitherto proposed, the present one, without satisfying all claims, nevertheless combines the greatest applicability with sufficient accuracy.—Liebig's *Annalen*, March 1848.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 30, 1848.

(The Marquis of Northampton, President, in the Chair.)

"Chemical Researches on the Nature of Wax." By Benjamin Collins Brodie, Esq.

It is known that bees'-wax is separable, by means of boiling alcohol, into two portions: to the one, which is more soluble in alcohol than the other portion, the name of *Cerine* has been given: the residuary portion, which does not dissolve, has been termed *Mycicine*. In this paper the author gives an account of his investigation of the properties of the former of these substances, namely Cerine.

This substance has been represented by certain chemists in France, M. Lewy and M. Gerhardt, as being convertible by oxidation into stearic acid, and as being a substance which stands with respect to that acid in the remarkable relation of an aldehyde. These views the author believes are incorrect; and he states that no pure chemical substance was procured by these chemists from cerine, and that the substance of which the greater part of the cerine consists is no aldehyde, but a hydrated acid, existing as such in bees'-wax.

The acid is best prepared by precipitation from the alcoholic solution of the cerine by an alcoholic solution of acetate of lead, and subsequent separation and precipitation of the acid by methods described in the present paper. When purified, the acid is a white brittle body, of a crystalline appearance, melting at from 79° to 80° C. The formula of the acid is $C_{54}\,H_{54}\,O_4$, a formula which was determined by the analysis of the silver salt having the constitution $C_{54}\,H_{53}\,O_3 + AgO$, and of the compound ether $C_{58}\,H_{58}\,O_4 = C_{54}\,H_{53}\,O_3 + C_4\,H_5\,O$. The acid is volatile: it was analysed after distillation; and it was also procured from the wax itself in a pure state by simple processes of crystallization. To this acid the author gives the name of *Cerotic acid*.

By the action of chlorine, the wax acid is converted into a substance having all the appearance of a gum-resin; a change analogous to which may be effected in various other wax substances examined by the author. It has still the characters of an acid, and has the formula $C_{54}\left\{\begin{matrix}H_{42}\\Cl_{12}\end{matrix}\right.O_4$, a formula which is confirmed by that of the compound ether $C_{58}\left\{\begin{matrix}H_{46}\\Cl_{12}\end{matrix}\right.O_4$. The analyses of these substances are given.

When distilled in a pure state, the cerotic acid is volatile. When

mixed with other waxy matters, however, it passes by distillation entirely into volatile oils, a circumstance which accounts for the fact that it has never been found dissolved in the wax distillate. By precipitating a weighed quantity of wax by acetate of lead, the quantity per cent. of the cerotic acid in the bees'-wax, namely 22, was determined.

This acid was present in all the European bees'-wax examined by the author; but suspecting that its quantity might vary in other instances, he procured bees'-wax from Ceylon, formed under different conditions of climate and vegetation, and found on examination that there was a total absence of the acid in that specimen. The author draws attention to this curious variation in the nature of an animal secretion under different conditions of life, a variation of which we have another example in that of the volatile acid of butter, discovered by Lerch*; namely, that the butyric and caproic acid of one season were, in another, replaced by vaccinic acid, differing from the former acids in the amount of oxygen alone.

May 11, 1848.

(The Marquis of Northampton, President, in the Chair.)

"On the Chemical Nature of a Wax from China." By Benjamin Collins Brodie, Esq.

The wax which is the subject of this investigation, is a substance imported into this country from China. It has the general appearance of spermaceti, but is harder than that body. The author gives reasons for believing that this wax, like bees'-wax, is a secretion from an insect.

The wax may be decomposed by fusion with hydrate of potash, by which process two substances are procured; namely, a wax acid, which, combined with the potash, forms a soap; and another body which is dissolved in the soap solution. By precipitation with chloride of barium and washing out the dried baryta salt with ether, or other suitable solvents, the two substances may be separated.

The substance dissolved in the ether has the appearance of a wax. By crystallization its melting-point may be raised to 79° C., at which point it is fixed. The body, when analysed, gave numbers agreeing with the formula $C_{54} H_{56} O_2$, the formula, namely, of the alcohol of cerotic acid, the acid which in a previous paper the author has shown to exist in a free condition in bees'-wax, and the constitution of which he there determined. To this alcohol the author gives the name of *cerotine*. By oxidation, by means of lime and potash, the alcohol is capable of being converted into cerotic acid, $C_{54} H_{54} O_4$. The analyses of the acid and of its silver salt are given. The formula of the alcohol is further confirmed by the analysis of its combination with sulphuric acid; and the process to be employed to procure this substance is detailed. Its formula is $SO_3, C_{54} H_{55} O + HO$; the sulphate of the oxide of cerotyle, using the usual chemical language to express the nature of the combination. By the action

* Chem. Gaz., vol. ii. p. 377.

of chlorine on the alcohol, the alcohol-type is destroyed, and a body is formed, analogous to chloral, containing two equivalents of hydrogen less than the alcohol itself. The analyses lead to the formula $C_{54}\left\{\begin{matrix}H_{40}\\Cl_{134}\end{matrix}\right. O_2$. The substance has the appearance of a resin.

By decomposing the above-mentioned baryta salt, after the cerotine has been entirely removed by washing with suitable solvents, the same cerotic acid may be obtained as that into which the alcohol itself is converted by oxidation. The analysis of the acid and of its silver salt is given.

This Chinese wax cannot be distilled without decomposition. By its distillation two substances are procured; cerotic acid, $C_{54}H_{54}O_4$, and hydrocarbon. The hydrocarbon consists principally of a solid matter, one of those substances which, in the opinion of the author, have been indiscriminately classed together under the general name of *paraffine*. This substance, to which he gives the name of *cerotine*, contains equal equivalents of hydrogen and carbon, and has the formula $C_{54}H_{54}$. This formula is determined with precision by the action of chlorine on the substance, which gives rise to a series of products of substitution, of which several were analysed, namely the substances

$$C_{54}\left\{\begin{matrix}H_{35}\\Cl_{19}\end{matrix}\right.,\quad C_{54}\left\{\begin{matrix}H_{33}\\Cl_{21}\end{matrix}\right.,\quad C_{54}\left\{\begin{matrix}H_{32}\\Cl_{22}\end{matrix}\right..$$

The density of the vapour of cerotine cannot be taken, as, by distillation, it is decomposed. The experiment was made of distilling and redistilling the substance in a sealed tube, in which cases it passes entirely into fluid and gaseous hydrocarbon.

The analysis of the Chinese wax itself corresponds with the formula $C_{108}H_{108}O_4$, which admits of a simple explanation of the nature of its decompositions: its decomposition by potash being explained by the equation

$$C_{108}H_{108}O_4 + KO\,HO = (C_{54}H_{53}O_3 + KO) + C_{54}H_{56}O_2,$$

and its decomposition by heat by the equation

$$C_{108}H_{108}O_4 = C_{54}H_{54}O_4 + C_{54}H_{54},$$

the substance itself belonging to the class of compound ethers.

The author announces his intention of following up this paper by a third on the constitution of myricine.

PATENT.

Patent granted to Charles de la Salzede, Paris, ***for Improvements in brassing and bronzing the Surface of Steel, Iron, Zinc, Lead and Tin.***

This invention consists in certain methods of coating steel, iron, zinc, lead and tin with brass and bronze.

In order to coat metal surfaces with brass, a bath is prepared, composed of the following ingredients:—5000 parts by weight of

distilled water, 610 parts of subcarbonate of potash, 25 parts of chloride of copper, 48 parts of sulphate of zinc, 305 parts of nitrate of ammonia, and 12 parts of cyanide of potassium. The cyanide of potassium is dissolved in a small portion (about 120 parts) of the cold distilled water; at the same time the subcarbonate of potash, chloride of copper and sulphate of zinc are introduced into the remaining portion of distilled water (contained in a separate vessel, and having its temperature increased from 144° to 172° F., to facilitate the solution of these matters); and when they are perfectly dissolved, and the solution has become cool, the nitrate of ammonia is added. After the solution has been shaken for a long time, it is allowed to stand for twenty-four hours; it is then decanted with a siphon, and the solution of cyanide of potassium (which should be limpid) is added thereto. If the solution thus prepared be submitted for about five hours to the action of a voltaic battery with a rapid current (such as Bunsen's, Grove's or Daniell's battery), and at a mean temperature of 77° F., it will deposit a coat of yellow copper or brass on the metal article immersed therein. This process may be performed in vessels of porcelain, china, glass or wood (which may be lined with bitumen, or any isolating resinous matter); and the vessels are preferred to be of a rectangular shape.

If the articles are to be coated with bronze, 25 parts of chloride of tin are to be substituted for the above-mentioned 48 parts of sulphate of zinc; the proportion of chloride of copper is to be increased from 25 parts to 48, and a plate of bronze is to be used as the electrode; in other respects the bath is prepared with the same ingredients, in the proportions above stated, and the process is conducted in the manner before described.

A bath for coating articles with brass is prepared by dissolving 500 parts of subcarbonate of potash, 15 parts of chloride of copper, 35 parts of sulphate of zinc, and 50 parts of cyanide of potassium together in 5000 parts of cold distilled water; after the bath has been stirred, it is allowed to stand for from twenty-four to forty-eight hours; it is then subjected, in a cold state (from 25° to 30° F.), to the action of the voltaic battery, during the same time and in like manner to the preceding baths. When this bath becomes impoverished by use, the salt of zinc or copper which has been absorbed must be replaced.

The bath last described may also be used for bronzing, by substituting about 10 parts of chloride of tin for the 35 parts of sulphate of zinc, and employing an electrode of bronze.

The patentee states that "in either of the processes above described, instead of the sulphate of zinc or chloride of tin, any neutral salts of zinc or tin may be employed, according to whether the article is to be covered with brass or bronze, so long as the bath is sufficiently rich in potash that there may be no action upon blue paper of turnsol." The proportions of the salts of tin, zinc and copper may be varied according to the colour desired to be given to the metal coating. This invention may also be applied to the coating of alloys.—Sealed September 30, 1847.

THE CHEMICAL GAZETTE.

No. CXXXVI.—June 15, 1848.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Changes which Organic Substances in particular experience in their Passage into the Urine. *By* F. WÖHLER *and* F. FRERICHS.

THE changes which substances introduced into the animal system experience in their passage into the urine are of considerable physiological interest, especially in regard to the doctrine of the metamorphosis of the constituents of the system; because we may expect through them to become more accurately acquainted with the chemical forces, which are active in the organism, especially in the blood, during this metamorphosis. Now this is especially the case when organic compounds are introduced of known chemical constitution, which have been accurately examined in every direction, and whose changes consequently admit of conclusions being drawn as to the cause producing them.

To obtain general results, long series of experiments are requisite, experiments which require considerable time for their performance, and are not free from peculiar difficulties. The following notices are contributions of this kind, which for the present may be looked upon as simple facts. The mode of experimenting consisted in either giving the animals, mostly dogs, the substances mixed with their food, or introducing them into the stomach by means of an elastic tube; they were then confined in a case lined with sheet-iron, the perforated flooring of which was provided with a funnel, which ensured the whole of the urine being collected. It is evident that we are not thus able to determine the locality of the metamorphosis, whether it takes place in the stomach and intestinal canal or in the blood, or, which is not very probable, in the kidneys. For the present this question may be left out of consideration.

It must moreover be remarked, that the effects of the substances introduced upon the system, their poisonous or non-poisonous properties, were observed with the greatest possible care.

1. *Salicylous Acid.*—This substance, which is isomeric with benzoic acid, was frequently given to dogs in doses of from ½ to 4 grms. It has a very irritating action upon the mucous membrane, but is not poisonous. The animals became at first restless and frothed at the mouth, but soon recovered completely. No trace of hippuric acid could be detected in the urine; it always contained, whether

small or large doses had been administered, unaltered salicylous acid, characterized at once by the intense violet colour which the urine assumed on the addition of perchloride of iron.

Salicylic acid, into which it might have become converted, was sought for in vain.

2. *Oil of Bitter Almonds free from Prussic Acid.*—The statements respecting the effects of this substance upon the animal system are at variance. Robiquet found it to be innocuous; Vogel, on the contrary, observed poisonous effects; and Dr. Pereira, who performed a series of experiments with it, observed symptoms of poisoning, which soon terminated fatally. With 4 drops of oil of bitter almonds which had been three times rectified, rabbits were deprived of sensation, began to respire quickly and with difficulty, but gradually came to again.

The experiments which we made upon dogs and rabbits with oil of bitter almonds perfectly free from prussic acid, proved decidedly that it is perfectly harmless. 2 grms., given to a small dog, irritated the mucous membranes with which they came in contact, caused salivation and frothing at the mouth like all essential oils, but produced no symptoms of poisoning. The animals drank a large quantity of water, and were then as lively as before. The urine which subsequently passed was very acid, and on evaporation became turbid, from the separation principally of square octahedrons of oxalate of lime. The concentrated liquid deposited, on the addition of muriatic acid, a large amount of hippuric acid.

According to this, oil of bitter almonds is converted in the animal system, by the assimilation of 2 atoms of oxygen, into benzoic acid, which again is changed into hippuric acid. The poisonous effects, noticed by former observers, must be ascribed to the oil not having been free from prussic acid.

3. *Amygdaline.*—This, as resulted from the earlier experiments of Buchner, is not poisonous; there is consequently no substance in the living system which can act the part of emulsine. In two cases only in which considerable doses were given to dogs, in the one case 3 grms. to a young dog, in the other 5 grms. to a full-grown animal, the following remarkable symptoms were observed:—The animals, which at first were as lively as before, became very ill; they vomited, respiration became slow and stertorous, and the extremities appeared completely paralysed. These symptoms continued without any alteration from six to eight hours, upon which the animals gradually awoke from their drowsiness, and were soon well again. May not, in this case, a slowly progressive transformation of at least a part of the amygdaline have taken place? The symptoms presented by the animals were those of poisoning by prussic acid, remarkable solely from their remaining for a long time at the same height without causing death. The food which the animals had taken could not have been the cause of this different behaviour; one dog had previously taken no food, the other only some coarse bread as usual. In both cases the breath smelt distinctly of prussic acid. On the addition of some emulsion of almonds to the urine, the same odour

was more strongly developed; consequently a portion of the amygdaline must have been separated unaltered by the kidneys. No hippuric acid could be detected in the urine.

In the other cases, where equally strong doses of amygdaline were administered, no symptoms of poisoning were apparent, nor could any odour of prussic acid be detected. No amygdaline could be detected in the urine, and hippuric acid was sought for in vain.

4. *Benzoic Æther.*—2 grms. were injected into the stomach of a dog, and produced decided symptoms of complete drunkenness. The animal fell about, lay for some minutes perfectly stupid, then rose again, reeling first on one side and then on the other. It was all over in the course of ten minutes. The urine was strongly acid; a portion was concentrated by distillation to a syrupy consistence. No benzoic æther could be detected in the distillate, which contained a large amount of carbonate of ammonia. Another portion, which was concentrated and mixed with muriatic acid, deposited a considerable quantity of hippuric acid. The benzoic acid of the benzoic æther had consequently become converted into hippuric acid, while the oxide of ethyle was lost in the system.

5. *Peruvian Balsam*, given to a dog, likewise caused the formation of hippuric acid, due to the cinnamic acid it contains. The urine, heated with muriatic acid, acquired a blood-red colour; it is evident therefore that some other substance passes with the hippuric acid into the urine, which is of some importance as regards the medicinal use of this balsam in diseases of the urino-genital organs.

6. *Tannic Acid.*—Pure tannic acid was administered to a dog in a dose of half a gramme, which was then gradually raised to 6 grms. The animal continued in health, but its stools gradually ceased, although its appetite remained the same. The urine had at first the normal yellow colour; subsequently it became darker, then deep brown, until at last it was brownish-black and perfectly opake.

Persalts of iron produced a blackish-blue precipitate, but no precipitate was obtained with solution of gelatine; the tannic acid had consequently become converted into gallic acid. Protosalts of iron likewise produced a bluish-black precipitate, showing the presence of pyrogallic acid. The ease with which the latter is converted, in the presence of ammonia (the urine had an alkaline reaction), into humus-like bodies, explains the origin of the blackish-brown colour which the urine at last possessed. It is remarkable that for three days after the last dose of tannic acid was given, the urine was of a dark colour, and reacted with salts of iron. The tannic acid is consequently converted, in its passage through the animal system, into gallic acid, pyrogallic acid and humus-like substances.

7. *Urates and Allantoin.*—These were purposely experimented with, in order to obtain some insight into the relation of uric acid to urea, and especially to decide the question whether uric acid is metamorphosed in the living system, in the same manner as for instance by peroxide of lead, into urea, oxalic acid and allantoin. This has been frequently assumed, and theories respecting the origin of the oxalic calculi based upon it; but this assumption has not been

supported by a single fact, for the conversion of uric acid by peroxide of lead shows, it is true, the possibility of such a reaction, but by no means proves that it really does take place in the living organism.

To obtain proof of the supposed formation of urea from uric acid, it being scarcely possible to determine with certainty the increase of a few grammes of urea in the urine of the dog or of man, $2\frac{1}{2}$ grms. of urate of potash were given to a rabbit, the urine of which had been previously frequently examined. The urea, the amount of which was very small before, often scarcely to be detected, was now found in considerable quantity; there was at least five times the amount. This experiment was repeated four times with the same result. A solution of 1·5 grm. of urate of ammonia was now injected into the jugular vein of a dog; no uric acid sediment was found in the urine, but numerous crystals of oxalate of lime.

A man who on the previous evening had taken a dose of urate of ammonia, passed the next morning urine of 1032 spec. grav., which deposited a grayish-white sediment, the chief mass of which consisted of oxalate of lime mixed with a slight trace of urate of ammonia. In another experiment, in which 4·5 grms. urate of ammonia were taken, a sediment was likewise formed, which consisted of oxalate of lime and some epithelial scales. This urine also possessed a very high specific gravity, and contained a large amount of urea.

Of the products of decomposition of uric acid, two, oxalic acid and urea, have been detected; the third, allantoin, was sought for in vain. On this account 4 grms. of allantoin were administered to a man, to ascertain what would be its products of metamorphosis. The expectation that it would be converted into oxalate of ammonia, as on boiling with caustic potash, was not confirmed. No oxalic acid could be detected in the urine, nor was any allantoin present as such. Another experiment, in which 6 grms. of allantoin were taken, led to the same negative result.

It results from these experiments, that uric acid experiences in the living system the same metamorphosis as can be artificially produced by peroxide of lead; urea and oxalic acid are formed, and probably also allantoin, the presence of which however could not be detected, because the products of its further metamorphosis are not known.

These facts are interesting in several points of view; in the first place, the inverse relation of urea to uric acid, the diminution of urea with preponderating uric acid in fever, and the reverse proportion in the normal urine, become intelligible; in the second place, they throw considerable light upon the mode of formation of the oxalic calculi, which proves to consist in an oxidation of the metamorphic products of uric acid. The importance of these data in therapeutics is self-evident.

8. *Sulphocyanide of Potassium.*—This compound, as likewise the following, was experimented with principally in order to obtain some insight into the behaviour of sulphur, and to trace, if possible,

the still mysterious mode of origin of cystic oxide, which contains so large a quantity of sulphur.

Sulphocyanide of potassium, even when given in very minute quantity, was constantly found again as such in the urine. Even in large doses it did not exhibit the poisonous effects which had been observed by previous experimenters. It appeared however to diminish considerably the activity of the spinal marrow. A dog to which 5 grms. of sulphocyanide of potassium were administered, became totally lame; seminal filaments were detected in considerable quantity in the urine. Anatomical alterations in the spinal marrow, which were accordingly suspected, could not be discovered on dissection. There was merely congestion of the lumbar portion of the spinal chord.

9. *Oil of Mustard and Ammonia* produced just as little poisonous symptoms as sulphocyanide of potassium; the urine always furnished sulphocyanide of ammonium. This metamorphosis was very frequently observed on rabbits, dogs and men. Oil of mustard is consequently decomposed in the living system in the same way as when heated with soda-lime, according to the discovery of Wertheim*.

What became of the allyle could not be ascertained; it does not give rise to the production of oil of garlic; the penetrating odour which characterizes the sulphuret and oxide of allyle could not be detected either in the breath or in the urine of the animals and persons who had taken the oil of mustard and ammonia.

In man, moderate doses of this compound produced excitement of the nervous system, sleeplessness, palpitation of the heart, &c. The organs of digestion were in no way affected by it. An experiment made with it on a patient suffering with intermittent fever led to no result. Eight doses of 1 gr., given during the apyrexia, did not prevent the return of the fever.

10. *Quinone.*—This substance does not possess the poisonous properties which might have been suspected from its powerful odour and action upon the living membrane. No effects were perceptible in a dog to which 0·5 grm. had been administered, nor even when a larger dose of nearly 1 grm. was given. It could not be detected in the urine, nor could it be ascertained what had become of it.

11. *Aniline* is equally innocuous; it could not be detected in the urine.

12. *Carbolic Acid.*—This substance, which occurs in castoreum, and to which the latter owes its peculiar odour, produced very poisonous symptoms. Rabbits, guinea-pigs and dogs, to which a few drops diluted with water were administered, constantly died in convulsions in the course of one-quarter of an hour. On dissection, no important anatomical lesion could be observed in any of these cases from which death might have been explained.

It is possible that castoreum partly owes its medicinal virtue to the small quantities of carbolic acid it contains. Unfortunately it is scarcely possible to obtain certain information on this subject by

* See Chem. Gaz., vol. xii. p. 495.

experiments upon hysteric individuals. The few experiments which were made had favourable results; but, as is well known, persons subject to hysterics find themselves better after every new medicine. It is certainly highly desirable that a series of experiments should be made upon this point, as it is possible a very cheap substitute might be thus obtained for the expensive castoreum.

13. *Alloxantine*, administered in doses of from 5 to 6 grms. to human subjects, was not found again as such in the urine, nor could any alloxan be detected in it. The urine contained a very large amount of urea; it is probable therefore that the alloxantine is converted into this substance.

14. *Urea.*—3 grms. given to a man were not converted into carbonate of ammonia, as expected; the urine remained acid as before; the urea was probably again separated as such.

15. *Phosphorous Acid and Arsenic Acid.*

A series of experiments were made in 1844, by Weigel and Krug of Cassel, upon the effects which phosphoric acid, contaminated with phosphorous acid or arsenic acid, produces in the animal body, especially upon the mucous membrane of the stomach. The principal result of these observations, which were made upon rabbits, was, that pure phosphoric acid, administered in moderate doses, has not the least action upon the stomach; but when, on the contrary, it is contaminated with phosphorous acid, it produces inflammatory swellings of the mucous membrane of the stomach; and that containing arsenic acid, even to the small amount of one-twelfth of a grain, acts as a deadly poison.

The frequent occurrence of these impurities in the officinal phosphoric acid, and the peculiar diseases to which preparations of phosphorus, and especially of phosphorous acid in the manufacture of lucifer-matches, have given rise to for some years past, rendered the subject of sufficient importance to submit it to further examination.

The experiments here described were made with perfectly pure substances, prepared for this purpose, in order to obtain simple results.

Experiments with Arsenic Acid.

I. 2 grms. of a dilute solution of pure arsenic acid were introduced into the stomach of a half-grown rabbit. For two hours it continued perfectly well; the next morning it was found dead. A great amount of urine and excrements had passed; on dissection the texture of the stomach was found unaltered; only at some limited spots a slight injection of the vessels was perceptible; nor was anything abnormal observed in the small intestines, but in the large ones the fæces were quite thin; the mucous membrane was of a very deep red colour.

II. 3 grms. of the same solution were given to a young dog. At first the animal kept perfectly quiet; it then began to vomit, and threw up in this manner a portion of the arsenic acid, although not to any large extent. It then recovered, and appeared for two hours

quite lively. It died, however, in the course of the night. Diarrhœa also occurred in this case.

The mucous membrane of the stomach was slightly reddened only at a few circumscribed places. The small intestine was coated with a white mucous stratum, which under the microscope appeared to consist solely of cylindrical epithelium. The large intestine was perfectly empty, and its mucous membrane of a deep red colour.

From these experiments it results that arsenic acid is certainly poisonous, but that its action is less intense than that of arsenious acid. The view hitherto adopted, that arsenic acid produces more violent effects, is not confirmed. Moreover, the mode of action of arsenic acid differs qualitatively in several points from that of arsenious acid. The first exhibits less locally irritating and caustic properties; its effects are more slow in making their appearance, and are probably produced in part by a reduction of the arsenic acid to arsenious acid in the intestinal canal. In favour of this view is the circumstance, that the appearances of local irritation occurred first in the lowermost part of the intestinal tract, while the upper portion, with which the poison must have come first in contact, was uninjured. Unfortunately, the amount of urine in the urinary bladder was too small to admit of the presence of arsenious acid (and not arsenic acid) being proved.

Experiment with Arseniate of Lime ($3CaO, AsO^5$).

The frequent occurrence of this substance in several mineral waters, and the fears expressed on this account by several persons, rendered it desirable to examine into its action upon the living organism.

3 grms. of pure arseniate of lime were given to a full-grown dog; at first it remained quiet, and after two hours exhibited no distinct symptoms of illness; the next morning, however, it was dead. In this case very liquid fæces had also passed off. In the stomach, which contained about 20 grms. of a mucous, faintly-acid liquid, coloured yellow by bile, numerous strongly-injected spots were visible; here and there ecchymoses of the size of a lentil were observed. The mucous membrane was reddened throughout the entire intestinal tract, but nowhere destroyed by inflammation.

The arseniate of lime consequently exerts, at least in *large doses*, poisonous effects, but probably owing solely to previous decomposition. It appears to be a stronger local irritant than dilute solutions of free arsenic acid.

Experiments with Phosphorous Acid.

I. A dilute aqueous solution of about 0·5 grm. of dry phosphorous acid was injected into the stomach of a pigeon. The bird at first continued unaffected, but in the course of a quarter of an hour it breathed with great difficulty, which however ceased occasionally. The animal then became very restless, with palpitation of the heart, fell upon its side, again rose, and finally died in the course of an hour. The lungs and air-passages, with the exception of some

strongly-injected spots of about the size of a pin's head, were perfectly healthy. The inner coat of the stomach was of a green colour, which however is frequently observed in birds. No traces of inflammation, as asserted by Weigel and Krug, were perceptible either in the glandular stomach or in any other part of the intestinal canal.

II. The same quantity was given to a guinea-pig; the animal was seized with convulsions, foamed at the nostrils, and death resulted in a few minutes. A portion of the liquid had got into the trachea, and had produced suffocation.

III. 1 grm. of phosphorous acid, in the state of a dilute solution, was injected into the stomach of a large cat. On withdrawing the elastic tube, a portion of the liquid appears likewise in this case to have found its way into the trachea. The animal was quiet at first, but soon began to breathe with difficulty and to foam; at a later period the breathing became still more difficult, and death resulted in thirty-six hours. In this case the stomach likewise appeared not to be essentially altered, nor was the intestinal canal; on the other hand, numerous inflammatory exudations had formed in the trachea and the bronchi. The lungs were in their normal state. It is difficult to decide how much these exudations, which probably owed their origin to some drops of the phosphorous acid having passed into the trachea, contributed to produce death. They were certainly not the sole cause; besides, they were entirely absent in the pigeon.

It results, from these experiments, that phosphorous acid possesses poisonous properties, but that the violent irritation described by Weigel and Klug does at least not always result.

It is interesting to find the analogy between phosphorus and arsenic shown even in their effects upon living beings. The lower oxides of both, arsenious and phosphorous acids, are most injurious, whilst the highest, arsenic acid, is at least comparatively mild and phosphoric acid innocuous.—Liebig's *Annalen* for March, 1848, p. 335.

On some Applications of Gutta Percha. By M. Vogel, Jun.

Several chemists have endeavoured to find solvents for gutta percha, and it was soon found to dissolve well in boiling oil of turpentine; but this solution in oil of turpentine presents several inconveniences, for when applied to marble, glass, &c., it dries slowly, and the surface is left somewhat viscous. It leaves stains upon paper, and the disagreeable odour of the turpentine is long in disappearing. As gutta percha is absolutely insoluble in alcohol, æther, acids, &c., I tried sulphuret of carbon, and I found that it dissolved readily in this medium, in every proportion, without the application of heat. When some drops of this solution are rubbed over any surface whatever, the sulphuret of carbon soon evaporates, and leaves a thin layer of gutta percha, which protects the object from the influence of water and of the air. On this account I have employed this solution to cover wounds occasioned by a sharp instrument; the sulphuret of carbon, evaporating upon the skin, pro-

duces considerable cold, and acts consequently as an antiphlogistic, causing the margins of the wound to unite. The sulphuret of carbon of commerce, however, frequently contains a trace of sulphuretted hydrogen, from which it must be freed before employing it as a solvent for the gutta percha; this is readily done by agitating the sulphuret with a small quantity of litharge or of carbonate of lead. It appears to me that a solution of gutta percha in sulphuret of carbon well deserves the attention of surgeons.

I have also employed this solution to cover fruits which it is desirable to preserve for collections of natural history; hitherto a coating of wax has been employed for the purpose; but great difficulty is experienced in removing the wax from the fruit without tearing the surface. The solution of gutta percha, which completely prevents the fruit from drying or becoming furrowed, has moreover this advantage, that the thin layer is easily removed by means of hot water.

By means of a few drops of this solution of gutta percha in sulphuret of carbon, bibulous paper may instantly be converted into writing paper, an object of some importance where any writing has been scratched out, as it renders these portions of the paper perfectly impermeable.

Lastly, this solution may be most advantageously employed for preserving paintings and drawings, as it has the property of fixing upon the paper any drawing made either with crayon, chalk or charcoal, so that it is no longer possible to efface the marks by rubbing. When some of the solution is spread over a drawing sketched with chalk, and it is then sprinkled with acid, there is no disengagement of carbonic acid, showing that the thin layer of gutta percha completely protects the drawings. There is no doubt that this solution of gutta percha in sulphuret of carbon will be found exceedingly useful to painters and draughtsmen for coating their cartoons, in place of the size which is usually employed.—*Journ. de Pharm.*, May 1848.

On a new Product of Decomposition of Urea.
By G. Wiedemann.

The author has found that, on exposing urea and nitrate of urea to a high temperature, both give rise to a new product of decomposition, which at a certain temperature is again decomposed into ammonia and cyanuric acid; and most probably, for this latter reason, had hitherto been overlooked in the examination of the products of decomposition of urea. At a temperature just above their melting-point urea and the nitrate pass into the substance $C^{12} H^8 N^8 O^4$, discovered by Liebig and Wöhler, and the new body. The latter may be regarded as a combination of 2 equivs. oxide of urene with 1 equiv. ammonia, and, as formerly mentioned in a brief notice*, may be called *Biuret*. The author moreover observed, that nitrate of urea, heated to 284°,

* Chem. Gaz., vol. v. p. 482.

disengages carbonic acid and protoxide of nitrogen, leaving a residue of nitrate of ammonia and urea. The acid which Pelouze found among the products of decomposition of the nitrate of urea by heat is cyanuric acid. Pelouze had stated that nitrate of urea is decomposed at 284°, and gave off a large amount of gas consisting of 2 vols. carbonic acid and 1 vol. protoxide of nitrogen, while urea and nitrate of ammonia form the residue. At a higher temperature further decomposition ensues; the urea is converted into carbonate of ammonia, and the nitrate of ammonia into protoxide of nitrogen and water, but no cyanuric acid is formed. The small amount of an acid found in the residue, the composition of which he left doubtful, was considered by him to be a new acid with apparently the formula $C^2 H^3 N^2 O^4$. Besides these experiments of Pelouze, there are some earlier ones by Fehling, showing that the nitrate of urea, kept for some length of time at 212°, melts and loses 12 per cent. in weight, disengaging carbonic acid and about half the volume of nitrogen. Fehling found in the residue from 30 to 40 per cent. of nitric acid, while nitrate of urea contains about 43 per cent.

The urea employed by the author for his experiments was prepared in part from urine and in part from ferrocyanide of potassium, according to Wöhler's method. Nitrate prepared from such material and dried at 122°, possesses the composition $C^2 H^5 N^3 O^8$.

On heating the nitrate of urea to 306°, it melts, and then disengages carbonic acid, nitrogen and carbonate of ammonia. As soon as these gases begin to escape, the temperature rises, even when the lamp is removed, to about 392°. In the residue is found a large amount of nitrate of ammonia, and about a twentieth of the nitrate of urea employed of the acid observed by Pelouze, but which, as above stated, is nothing but cyanuric acid, as will be seen from the following experiments:—

The residue was dissolved in water to which a little nitric acid was added, in order to expel the carbonic acid from the carbonate of ammonia contained in it. When the amount of water is not too large, the greater portion of the acid crystallizes from the solution on cooling. To obtain the remainder, the liquid is precipitated with basic acetate of lead, the precipitate decomposed with sulphuretted hydrogen, the collected deposit exhausted with hot water, filtered from sulphuret of lead, and the solution of the free acid evaporated to a syrup, when it is obtained on cooling in crystals, which are purified by recrystallization. The liquid filtered in this process from the precipitate with basic acetate of lead, contains any undecomposed nitrate of urea, and likewise the biuret, which, as will be shown further on, is readily detected from its behaviour towards oxide of copper and potash, with which it turns red.

The acid prepared according to the process just described possesses the following properties:—It forms prismatic crystals, which are tasteless, grate between the teeth, and dissolve sparingly in alcohol and cold water, more readily in hot water. The solution reddens blue litmus-paper. Heated upon platinum-foil, it is volatilized without leaving the least residue. It lost 22 per cent. of water at 212°, or

even on long desiccation over sulphuric acid. The substance, dried at 212°, furnished 27·94 carbon, 2·55 hydrogen, and 32·81 nitrogen, which numbers agree pretty accurately with those calculated according to the formula $C^6 H^3 N^3 O^6$. The amount of water found corresponds to 4 equivs., which requires 21·75 per cent. The acid, moreover, behaved exactly like cyanuric acid towards an ammoniacal solution of nitrate of silver, acetate of lead, ammoniacal solution of oxide of copper, and on dry distillation. Mixed with an ammoniacal solution of oxide of copper, cyanuric acid forms a violet precipitate, the cyanurate of oxide of copper and of the oxide of ammonium, which is very sparingly soluble in boiling water and ammonia and insoluble in cold water. This salt separates as a microscopic powder from the cold solution of the cyanuric acid in the ammoniacal solution of oxide of copper; from the hot solution, on the contrary, in brown shining laminæ, but only in small quantity. The analysis of this salt furnished—

Carbon.....	20·29	20·00	6	20·37
Hydrogen	3·18	3·18	5	2·83
Nitrogen	32·03	32·03	4	31·69
Oxygen	..	..	5	22·64
Oxide of copper	22·47	22·38	1	22·47

If cyanuric acid is bibasic, as results from the recent researches of Wöhler*, this salt will be represented by the formula

$$CuO, NH^4 O + C^6 H N^3 O^4.$$

Biuret, $C^4 H^5 N^3 O^4 + 2HO$ (crystallized from water), is, as above stated, contained in the liquid from which the cyanuric acid has been precipitated with basic acetate of lead. The excess of lead is removed from the solution with sulphuretted hydrogen and evaporated. The filtered liquid contains along with the biuret a small amount of nitrate of ammonia; the former, however, is far less soluble, and consequently separates first. It forms small white crystals.

The same substance is obtained when, instead of the nitrate, the pure substance is kept for some length of time fused between 302° and 338°. Ammonia, aqueous vapour and some carbonate of ammonia are evolved; subsequently the compound $C^{12} H^8 N^8 O^4$, discovered by Liebig and Wöhler, and which has subsequently been asserted by Gerhardt and Laurent to be ammelide, is deposited. On extracting the fused mass with water, the greater portion of the latter substance is left undissolved; acetate of lead precipitates from this solution cyanuric acid and the remainder of the ammelide; and the liquid now furnishes on evaporation the same substance as the nitrate of urea. It is characterized by its reaction with oxide of copper. The solution of a persalt of copper is coloured red when boiled with biuret and potash.

Biuret dissolves in cold concentrated sulphuric acid without any decomposition; for when the acid is saturated with carbonate of

* See Chem. Gaz., vol. v. p. 440.

baryta, it again separates unaltered. Nitric acid equally dissolves biuret without decomposition even on boiling; but it is decomposed by fuming nitric acid. Its solution in water is not precipitated by neutral acetate of lead, nor by an ammoniacal solution of nitrate of silver; indeed it does not appear to enter into combination with bases. Biuret dissolves readily in cold water, and still more easily in alcohol. The crystals which separate from the aqueous solution contain 15 per cent. of water, corresponding to the formula above given, which they part with at 212°. From alcohol it crystallizes in anhydrous plates. The analysis of the dried substance, crystallized either from water or alcohol, gave—

Carbon	23·19	23·19	23·30	23·37	23·42	4	=23·30
Hydrogen..	4·97	4·85	5·18	4·85	4·75	5	4·85
Nitrogen ..	40·59	40·58	..	..	..	3	40·77
Oxygen....	..	..	..	..	..	4	31·08

Biuret is formed in a very simple manner from urea, as shown by the following equation:—

$$C^4 H^8 N^4 O^4 \text{ (urea)} - NH^3 = C^4 H^5 N^3 O^4 \text{ (biuret)}.$$

Assuming that urea is composed of 1 equiv. oxide of ammonium and 1 equiv. cyanic acid, biuret may be regarded as a combination of 2 equivs. cyanic acid with 1 equiv. oxide of ammonium. If urea is considered, according to Berzelius, as a compound of ammonia and oxide of urene, $C^2 H N O^2 + NH^3$, biuret will appear as $2(C^2 HNO^2) + NH^3$; the name biuret has been chosen in accordance with this expression.

The product which is formed from biuret when its solution is mixed with a salt of the oxide of copper and boiled with potash, is obtained on evaporating the liquid in minute red crystals; but it was impossible to obtain sufficient to submit it to analysis.—*Journ. für Prakt. Chem.*, xliii. p. 271.

On the Action of Nitric Acid upon the Sulphocyanic Æthers. *By* Sh. Muspratt, *with Remarks by* C. Gerhardt.

Mr. Muspratt has examined the action of nitric acid upon the sulphocyanides of ethyle and methyle. The sulphocyanide of ethyle is violently acted upon by the nitric acid; nitrous acid, deutoxide of nitrogen and carbonic acid are given off, and at the same time sulphuric acid is formed, the quantity of which depends on the degree of concentration of the nitric acid used. If very weak acid was used and the distillation carried on slowly, mere traces of sulphuric acid were detected in the liquid. After the distillate had been returned four or five times into the retort, it was evaporated on the water-bath until the whole of the nitric acid was expelled; the residue had a disagreeable alliaceous odour, and was of the consistency of oil of vitriol; it was diluted with water and saturated with carbonate of baryta. The filtered liquid yielded on evaporation large crystals of a salt, to which Mr. Muspratt gives the name of hyposulphathylate of baryta. The crystals were dissolved in

water, precipitated by absolute alcohol, and purified by recrystallization. The acid is easily prepared from this salt by precipitating the aqueous solution with an excess of sulphuric acid, digesting the filtered portion with carbonate of lead, filtering, and decomposing with sulphuretted hydrogen. The filtered liquid, evaporated in the water-bath, furnishes the acid in a state of purity.

Hyposulphathylic Acid supports a very high temperature before decomposition, on which vapours of sulphuric acid and subsequently of sulphurous acid escape; it has, as well as its salts, a very disagreeable acid taste; it dissolves in every proportion in water and alcohol; all its salts are soluble. The residue obtained on fusing the acid with hydrate of potash liberates a large amount of sulphurous acid on the addition of sulphuric or muriatic acid.

The *baryta salt* is very soluble, and crystallizes only from concentrated solutions; the crystals are rhombohedral prisms. It is also very soluble in spirit and in æther, but insoluble in absolute alcohol, which precipitates it from its concentrated aqueous solutions in beautiful silky needles. It parts with all its water of crystallization at 212°. The dried crystals, on fusion with potassium, did not indicate the least trace of nitrogen. The analysis of the salt, dried at 212°, gave 13·76–13·16 carbon, 3·21–3·05 hydrogen, 17·99–17·56 sulphur, and 42·69–43·26 baryta, results which lead to the formula $C^4 H^5 S^2 O^5$, BaO. According to this the reaction which gives rise to the acid is expressed by the following equation:—

$$C^6 H^5 S^2 N + 2NO^5 + 4HO = 2CO^2 + C^4 H^6 S^2 O^6 + 2NO^2 + NH^3.$$

Mr. Muspratt adopts a far more complicated equation, in which both NO^2 and NO^4 simultaneously intervene; but the red vapours evidently arise from a subsequent oxidation of the NO^2. A determination of water of crystallization afforded 5·02 per cent., which is equivalent to $C^4 H^5 S^2 O^5$, BaO + HO.

When this salt is heated in a test-tube, it gives off at a high temperature aqueous vapours of a suffocating odour, and the black residue preserves for some time the properties of a pyrophorus.

Hyposulphathylate of Lead crystallizes from a hot concentrated solution in beautiful colourless tablets, which are very soluble in water and alcohol. When heated in a tube, it puffs up, blackens, and the residue then contains sulphate. At 212° it parts with 4·09 per cent. water; the dried salt contained 52·76 per cent. oxide of lead, leading to the formula $C^4 H^5 S^2 O^5$, PbO + HO.

Hyposulphathylate of Copper, $C^4 H^5 S^2 O^5$, CuO + 5HO.—This salt is very readily soluble, and consequently very difficult to obtain in crystals. When heated in a glass tube, it puffs up, and disengages, as soon as it becomes black, vapours of a very disagreeable odour. The salt, dried over sulphuric acid for several days, gave on analysis—

Carbon.....	13·09	4 =	300·0	12·90
Hydrogen	4·84	10	125·0	5·48
Sulphur	..	2	402·3	17·20
Oxygen	..	10	1000·0	42·92
Oxide of copper	21·68	1	495·7	21·50

The same acid is produced by the action of a mixture of hydrochloric acid and chlorate of potash upon sulphocyanide of ethyle.

Mr. Muspratt has also prepared, with the bisulphuret of ethyle, the acid of MM. Lœwig and Weidemann; the copper salt, dried at 212°, afforded carbon 14·48, and hydrogen 5·10 per cent., from which he calculates the formula $C^4 H^5 S^2 O^4$, CuO + 4Aq, and consequently admits that this salt differs from the compound previously described*. In my opinion Mr. Muspratt is in error. His new salts appear to me to be identical with the sulphosulphethylates; it will presently be seen that the analysis of the lead salt obtained with the homologous methylic compound confirms this opinion.

Nitric acid readily attacks the sulphocyanide of methyle; the acid obtained is without odour, and resists a tolerably high temperature; it is identical with that obtained by M. Kolbe by the action of zinc upon the chlorosulphuretted methylates. The *baryta salt* is very soluble in water, and is precipitated by alcohol from its aqueous solution. Dried at 212°, it contained 7·23 carbon, 1·58 hydrogen, 19·80 sulphur, and 46·74 per cent. baryta, leading to the formula $C^2 H^3 S^2 O^5$, BaO. The crystallized salt contains 1 atom of water.

The *lead salt* crystallizes in beautiful rhombic prisms, which part with 4·27 per cent. of water at 212°; they contain 53·39 per cent. oxide of lead, and are consequently represented by the formula $C^2 H^3 S^2 O^5$, PbO + Aq.

The *copper salt* is obtained in beautiful crystals on slow evaporation of the aqueous solution. The crystals dried over sulphuric acid contained 6·94 per cent. carbon, 4·99 hydrogen, leading to $C^2 H^3 S^2 O^5$, CuO + 5Aq.

Mr. Muspratt has likewise prepared the lead salt from the acid obtained with the bisulphuret of methyle; it crystallizes in beautiful rhombic prisms, which when heated disengage aqueous vapours of a very penetrating odour. The salt dried over sulphuric acid afforded on analysis 5·87 carbon, 2·01 hydrogen, and 54·33 per cent. oxide of lead, from which he deduces the formula $C^2 H^3 S^2 O^4$, PbO + Aq, which I alter to $C^2 H^3 S^2 O^5$, PbO. Mr. Muspratt's formula requires 6·1 C, 2·02 H; that which I propose, 6·03 C and 1·5 H. In fact, I believe that this salt is identical with the lead salt prepared from the sulphocyanide of methyle.

I am not inclined to look upon the salts described by Mr. Muspratt as belonging to a new class; they all form part of a homologous series, with the different terms of which we have already been made acquainted by the researches of Lœwig and Weidemann, Gerathewohl and Kolbe, viz.—

Sulphuretted metholates (sulphosulphomethylates) $C^2 H^3 S^2 O^5$ MO.
Sulphuretted ethylates (sulphosulphethylates) .. $C^4 H^5 S^2 O^5$ MO.
Sulphuretted amylates (sulphosulphamylates) .. $C^{10} H^{11} S^2 O^5$ MO.

Journ. de Pharm., April, p. 302.

* Mr. Muspratt's formula requires 14·20 carbon and 5·33 hydrogen. I consider the formula $C^4 H^5 S^2 O^5$, CuO + 3Aq, which requires 14·3 carbon, 4·8 hydrogen, as more correct. It should be observed that Mr. Muspratt only gives the analysis of the hyposulphathylate of copper dried over sulphuric acid; it was not dried at 212°, as was the salt obtained with the bisulphuret of ethyle.

On the Decomposition and partial Solution of Minerals, Rocks, &c. by pure Water, and Water charged with Carbonic Acid. By Prof. W. B. Rogers *and* Prof. R. E. Rogers.

It is matter of surprise that so little has hitherto been done to determine, by *actual experiment, the solvent power of water and of carbonated water* upon mineral compounds. The only results heretofore published on the subject, so far as we are aware, are the comparatively isolated experiments of Struve, Forchhammer, and Polstorf and Wiegmann, as cited by Liebig in the last edition of his 'Agricultural Chemistry'*. But these were of too restricted a scope to furnish a solid basis for reasoning *generally* on the disintegration of rocks, the formation of chalcedonic, zeolitic, and other minerals by solution, and the conveyance of inorganic materials into the structure of plants. Yet upon such slender experimental foundation rest the common theories of the decomposing and forming action of the meteoric waters.

It is obviously therefore a question of the first importance, to decide whether water, pure or charged with carbonic acid, possesses the *general* decomposing and dissolving power which some chemists have, vaguely and without sufficient evidence, ascribed to it, or whether this action is manifested only with the few materials hitherto tried, and which all contain an *alkali*.

To resolve this question has been the object of our labours; and we feel that we have been well-rewarded by the result, proving, as it does most conclusively, *the solvent and decomposing power of pure and carbonated water upon all the important mineral aggregates, as well without as with alkaline ingredients.*

Our experiments have been of two kinds,—1st, by an *extemporaneous method with the tache*; and 2nd, by *prolonged digestion* at the ordinary temperature.

In the former method, a small quantity of the mineral, some 5 or 10 grs., in *very fine powder*, is leached for a few moments on a small filter of purified paper, and a single clear drop of the liquid, received on a platinum slip, is dried and examined by appropriate tests before and after ignition. In the second process, a quantity (40 grs.) of the finely-powdered mineral is placed with a certain volume (10 cubic inches) of the liquid in a green glass bottle, and agitated from time to time for a prescribed period. The liquid separated by filtration is evaporated to dryness in a platinum capsule. The residuum is then critically examined, and, if in sufficient amount, is submitted to quantitative analysis.

In both processes *two parallel experiments* are made, the one with pure de-aërated water, the other with water charged to saturation at 60° with CO^2. In the second process, the alkali, lime, &c., which may be dissolved by action on the containing glass, are determined by parallel experiments, with bottles of the same kind, charged, the one with simple water, the other with carbonated water, and exposed

* See also a valuable memoir on the solubility of fluoride of calcium in water, &c., by G. Wilson, M.D., Chem. Gaz., vol. iv. p. 183.

to the solvent action for the same time and with the same agitation as those containing the powdered minerals.

The following is a list of the minerals and other substances which we have subjected to *the analytic action of pure water and of carbonic acid water*:—

Potash felspar, 3 var.	Chlorite, 2 var.	Brown garnet.
Soda felspar.	Talc, 2 var.	Dolomite.
Lithia felspar.	Serpentine.	Flint glass.
Glassy felspar.	Steatite.	Green bottle-glass.
Labradorite.	Olivine.	Green German glass.
Mica, 2 var.	Hypersthene.	Hard white Bohemian glass.
Leucite.		
Analcime.	Hornblende, 2 var.	Wedgewood mortar.
Mesotype.	Actinolite.	Chinese porcelain.
Scolecite.	Tremolite.	
Schorl, 2 var.	Augite.	Anthracite.
Greenstone, 2 var.	Asbestus, 2 var.	Bituminous coal.
Chalcedony.	Coccolite.	Lignite.
Obsidian.		Charcoal.
Lava.	Epidote massive.	Ashes of coal and wood.
Gneiss.	Epidote crystals, 2var.	
Hornblende slate, &c.	Axinite.	Woods.
Soils.	Prehnite.	

1. By the tache process we find *that all the minerals and glasses in this list are partially decomposed and dissolved by carbonated water, and most of them also by pure water.*

When the substance is *very minutely powdered*, before mingling it with the liquid, even the first drops that pass the filter will commonly give a tache containing some of the alkali or alkaline earth that has been dissolved. In this way proof of the solvent power of the *carbonated water* may generally be obtained in less than ten minutes after adding it to the powder. As the action is continued, by returning the liquid to the filter, the effect is increased. In the case of *simple water*, the result is much feebler, and requires a longer time. But with nearly all the substances enumerated it is entirely unequivocal, and with some of them quite intense.

2. It is interesting to observe how from *a single drop* of the clear filtered liquid we obtain *distinctive* evidence of the presence of *alkalies or lime or magnesia.* The latter are indicated by the milkiness of the drop when reduced by evaporation on the platinum slip, as well as by the volume and whiteness of the tache. But further and more minute information is obtained by testing the tache before ignition, and again at successive stages of ignition. The *volatility* of the *three fixed alkalies* and their carbonates we have found to be much greater than seems to be generally imagined. By carefully comparing them in this respect with one another and with lime and magnesia, we have been enabled to make very advantageous use of the blowpipe, in connexion with test-paper, in examining the tache, so as to recognise the alkalies and alkaline earths severally present in

the tache of felspar, hornblende, serpentine, epidote, and other minerals.

These and other habitudes of the tache obtained with carbonated water give this method unexpected value in the *quantitative analysis of minerals. It furnishes by far the easiest and most speedy method of discerning the presence of an alkali, or lime, or magnesia in a mineral*; and we think therefore that it promises to become a useful auxiliary to the mineralogist in connexion with the ordinary blow-pipe reactions.

3. By the *second method*, that of prolonged digestion, we have actually made with carbonated water, and even with simple water, *a partial analysis of a number of complex minerals.* The specimens exposed to the CO^2 water for forty-eight hours, and to the simple water for one week, have in many instances furnished a sufficient amount of material to the liquid to admit of a quantitative examination. Thus from *hornblende, actinolite, epidote, chlorite, serpentine, felspar, mesotype*, &c., we have procured a quantity of *lime, magnesia, oxide of iron, alumina, silica* and *alkali, the dissolved ingredients of these minerals severally amounting to from* 0·4 *to* 1 *per cent. of the whole mass.* The lime, magnesia and alkalies are in the form of carbonates; the iron, in the case of hornblende, epidote, &c., passing from the state of carbonate to that of peroxide during the evaporation, collects in brown flocculi, along with the silica and alumina, at the bottom of the capsule. Thus, 40 grs. of hornblende, digested for forty-eight hours in CO^2 water at 60°, with repeated agitation, yielded,—silica, 0·08; oxide of iron, 0·05; lime, 0·13; magnesia, 0·095; manganese, a distinct trace.

4. Most of the substances above enumerated, when finely powdered in an agate mortar and moistened with pure water in a platinum capsule, *give a decided alkaline reaction with test-paper properly prepared.* Among the materials presenting this effect most strongly are serpentine, chlorite, tremolite, asbestus, mica, hornblende, the felspars and glass. The effect is especially striking with powdered glass. But it is important to note that *this reaction is more immediate and stronger with the magnesian and calcareo-magnesian silicates than with the felspars and most other alkaline minerals.*

In making this and all the other experiments embraced in the present inquiries, it is of course necessary that the specimen should be free from any adhering carbonate of magnesia or lime, either of which would give rise to an alkaline reaction, and the former in quite a marked degree. It is moreover necessary to avoid using either a Wedgewood or glass mortar, as the abraded matter would in such case give to the carbonated water a very perceptible amount of alkali.

5. The comparative readiness with which the *magnesian and calcareo-magnesian silicates* yield to the decomposing and dissolving action of carbonated and even simple water, *is we believe a fact no less important than it is true.* It explains the rapid decomposition of the rocks composed mainly of hornblende, epidote, chlorite, &c., without calling in the agency of an *alkali*; and it accounts for the

fact that rocks of this kind are often much more rapidly decomposed by meteoric actions than even the felspars themselves. It enables us moreover to trace the simple process by which plants are furnished with the lime and magnesia they require, from soils containing these silicates, without our having recourse to any mysterious decomposing power of the roots of the growing vegetable.

6. Among the points of interest incidentally determined during these investigations, may be mentioned the curious and instructive fact, that *anthracite coal, bituminous coal* and *lignite*, treated by the tache process, *give unequivocal evidence of alkali*, while the *ashes* of these materials, similarly treated, yield *no trace of alkali.* It thus becomes evident that the absence of alkali in the ash of these combustibles, instead of being a consequence of its absence in the coal itself, is really due to the *high temperature at which the ash is formed.* We have here the explanation of a fact, which might otherwise appear inconsistent with the admitted vegetable origin of coal.

7. Another incidental result of interest is, *the extraction of carbonate of potash from wood* by leaching it in fine powder with carbonated water. This effect we have found to be quite distinct with maple, oak, hickory, &c. Hitherto the opinion appears to have prevailed, that the alkali or its carbonate could only be eliminated by the *incineration* of the vegetable material.

From the great rapidity with which, according to our experiments, potash and soda and their carbonates, but especially potash and its carbonate, rise in vapour at a strong red heat, we are persuaded that *a large error must be committed in estimating the amount of these materials contained in plants by the results of incineration*; and we believe that in not a few cases the quantity obtained is scarcely one-half of what really exists in the vegetable mass. The important bearing of this consideration upon the late numerous and elaborate analyses of ashes should we think claim the special attention of chemists. Indeed it seems a little remarkable that the source of error here referred to has not already been brought to the notice of analysts, as likely to modify materially their results.—Silliman's *Journal*, May 1848.

ANALYTICAL CHEMISTRY.

On the Analysis of Chrome Iron Ore. By T. S. Hunt.

This mineral is well known to be most difficult of decomposition by the processes generally employed, which consist in fusing it with a mixture of nitre and hydrate of potash or an alkaline carbonate. In these, however finely the ore is pulverized, a portion almost invariably escapes decomposition. To obtain the mineral in a state of minute division, Fresenius recommends elutriation, and directs that after fusion with nitre and carbonate of soda, the portion insoluble in water be digested with hydrochloric acid, and the amount of undecomposed ore be deducted from the original quantity.

This may serve for the analysis of pure homogeneous specimens, but the common varieties are generally more or less mixed with foreign substances, and often with silicates of alumina and magnesia, which are lighter than the ore; in the process of elutriation, consequently, the portion of finely-divided ore obtained suspended in the water will contain a larger proportion of the impurities than that which remains at the bottom of the vessel. Again, when the powder thus obtained is fused with an alkaline carbonate, the silicates are at once attacked, while the portion which remains to be deducted after the action of both alkalies and acid, is pure chromate of iron. In this way a specimen of impure ore will give a per-centage of oxide of chromium considerably below the truth.

While endeavouring to find some more eligible mode of treatment, it occurred to me that the bisulphate of potash might be used with advantage, and in this I was not disappointed, for I found that with certain precautions the mineral might be completely decomposed by it. The chromic iron must first be very finely lævigated (a gramme of the crushed ore will require fifteen or twenty minutes trituration in an agate mortar); it is then to be mixed with ten or twelve times its weight of fused bisulphate of potash, and the mixture heated to fusion in a platinum crucible and preserved at a gentle red heat for about thirty minutes. The crucible and its contents when cold are placed in water, which with the aid of heat soon dissolves the saline mass. The greater part of the chromium is left as a green basic sulphate, insoluble in water or hydrochloric acid, and apparently identical with that obtained when any salts of chromium are heated with an excess of strong sulphuric acid.

The best mode of treating this mixture of soluble and insoluble salts is, to boil the whole for a few minutes with an excess of carbonate of potash or soda, which precipitates the alumina, iron, and chromium, that may be in solution, and decomposes the insoluble sulphate; it is not easy, however, in this way to remove all the sulphuric acid, and thus render the residue quite soluble in hydrochloric acid; but this is of no importance. The dried precipitate is now to be treated after the process recommended by Fresenius, which consists in fusing it with five times its weight of a mixture of equal parts of nitre and carbonate of soda. The operation should be performed in a platinum, or rather in a silver crucible over a spirit-lamp, and the mixture kept in fusion ten or fifteen minutes, to ensure the perfect solution of the chromium. The chromate of potash is then dissolved out from the mixture of oxide of iron, alumina and magnesia, which may be separated in the ordinary manner; if the precautions above mentioned have been observed, no trace of undecomposed ore will be left after treating the mixture with hydrochloric acid. A small portion of magnesia remains dissolved in the filtrate from the precipitate by carbonate of soda, and may be obtained by evaporating to dryness. Any silica which the mineral contained is also dissolved, and may be separated in the usual manner.

The presence of a small portion of sulphates prevents the deter-

mination of the chromic acid by a salt of lead; we accordingly supersaturate the solution with hydrochloric acid, and boil with alcohol to convert it into chloride of chromium, from which the oxide is to be precipitated by adding ammonia in excess and boiling for a few minutes.

I have employed this method several times with perfect success; it is easy of execution, and being free from any sources of error, yields very accurate results.—Silliman's *Journal*, May 1848.

Absorption of Carbonic Acid by Sulphuric Acid.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—Having read in your Journal of March the 15th, the extraordinary discovery of Profs. W. B. and R. D. Rogers, that sulphuric acid at 60° F. absorbed 94 per cent. of carbonic acid, and also seen in the Number for May the 1st some experiments by Mr. Noad, proving that even if sulphuric acid had this property, it did not in any way interfere with the analysis of carbonates invented by Fresenius and Will, I was led to perform the following experiment, for which you will perhaps find room in your Journal. I introduced into a Liebig's potash-bulb sulphuric acid, spec. grav. 1·82 at the temperature of 60° F., and weighed it, the weight of the bulb being 256·32 grs., the weight of the bulb and acid 642·02 grs., making 385·70 grs. of acid. I then connected the bulb with a long chloride of calcium tube, and passed a stream of carbonic acid gas through the apparatus for one hour; the open end of the potash-bulb had also a chloride of calcium tube attached to it, to prevent the acid absorbing any moisture from the air, and the gas was perfectly dry. On again weighing, I found no difference in weight; and on neutralizing a portion of the acid with ammonia and adding lime-water, there was no precipitate, nor even the slightest turbidity; so that if carbonic acid is absorbed by sulphuric acid, it neither adds to its weight, nor will it when in solution form carbonate of lime, both of which seem quite incomprehensible. It may be as well to add, that the experiment was performed with a delicate balance made by Oertling of London, and the carbonic acid was set free from carbonate of lime by dilute hydrochloric acid, so that no absorption could have taken place in the evolution flask.

I am, Sir,

Your most obedient Servant,

35 Michael's Place, Brompton. Reginald J. Morley.

Mode of detecting Neutral Carbonated Alkali in Bicarbonate.

Chevallier recommends the following method:—Starch-sugar is added to the aqueous solution of the bicarbonate under examination, and the mixture heated; if any neutral carbonate is present, the mixture turns yellow or brown.—Liebig's *Annalen*, Dec. 1847.

THE CHEMICAL GAZETTE.

No. CXXXVII.—July 1, 1848.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Nitrates of Mercury. *By* C. GERHARDT.

IT is well known that hyponitric vapours instantly attack metallic mercury, and convert it into a salt. Several chemists conclude, from the nitrogen substitutions in organic substances, that the hyponitric vapours behave under these circumstances as a simple body, combining directly with the mercury according to the equation

$$NO^4 + Hg = NO^4, Hg = NO^3, HgO.$$

The experiment can never have been made, for I have assured myself that the reaction is a totally different one.

When hyponitric vapours are passed into a balloon containing mercury and immersed in ice, the whole of the metal is converted into a perfectly white powder, which consists of protonitrate of mercury; but simultaneously, and during the entire duration of the operation, deutoxide of nitrogen is liberated. I have ascertained by reagents that no trace of nitrite is formed. This reaction is explained by the following equation:—

$$2NO^4 + 2Hg = NO^5, Hg^2\,O + NO^2.$$

If the nitrate thus formed is triturated with a small quantity of water, and the mixture is heated to boiling, small, but very brilliant oblique rhombic prisms of subnitrate of mercury are obtained on cooling. These crystals contain

$$NO^5\,Hg^2\,O + Hg^2\,O, HO.$$

Upon this occasion I made some experiments on the composition and formation of the protonitrates of mercury in general; and I am convinced that the results recently communicated to the Academy by M. Lefort are not quite accurate, owing to the mode of analysis employed by that chemist. The nitrate and the two subnitrates of the protoxide of mercury contain the elements of water, which M. Lefort estimated by the difference found on weighing together the mercury and water, and then determining the amount of mercury. Now by this method the amount of mercury is always from 1 to 2 per cent. too low; for instance, M. Lefort obtained 69·98 and 69·06 per cent. of mercury for the nitrate, while I have found 71·3 per cent., which agrees perfectly with the formula $NO^5\,Hg^2\,O + 2HO$, which requires 71·4 per cent. It will be ob-

served that the nitrate has a similar composition to the subnitrate, the hydrate of the protoxide of mercury being replaced by water; the amount of water is easily determined in these salts, with a few precautions, by the process employed for organic analysis; heated to 572° F., they leave perfectly pure peroxide of mercury, the proportion of which gives very accurately the quantity of mercury they contain.

The nitrate is obtained in hexagonal tablets or rhombohedral crystals whenever mercury is dissolved in an excess of dilute nitric acid, or a subnitrate of the protoxide is dissolved in this medium; a supernitrate is never obtained even in the presence of a large excess of nitric acid. The subnitrates are produced by the action of water upon the nitrate. If crystals of this salt are dissolved in a little water, and heated to boiling, the new crystals, which are deposited on cooling, consist of the subsalt, the composition of which is given above. When a larger quantity of water is used, a yellow insoluble subsalt is produced, which subsequently turns black, being finally converted into mercury and peroxide. This subsalt appears to correspond to the white subnitrate of the peroxide of mercury recently analysed by M. Millon, $NO^5\ HgO + 2HgO$. My own analyses confirm the accuracy of this formula. The orange or yellow subnitrate of the peroxide of mercury of Sir Robert Kane does not exist; it is simply the peroxide of mercury, the colour of which varies between yellow and orange, accordingly as obtained by the action of water or by that of heat, upon the nitrate of the peroxide of mercury.

The crystallized subnitrate of the protoxide of mercury, the composition of which I have indicated above, corresponds to the crystallized subnitrate of the peroxide of mercury, $HgO, NO^5 + HgO, HO$. It is likewise produced when a solution of the nitrate in nitric acid is kept boiling for some time, and the nitric acid which is evaporated replaced by water. There is also frequently obtained under these circumstances flattened prisms of a subnitrate, of the composition of which I am still doubtful.

The nitrate of the protoxide of mercury experiences a remarkable metamorphosis when heated, which has been very erroneously interpreted by chemists. It melts at 212°; and if the heat is maintained, it liberates water and nitric acid, nitrous vapours and deutoxide of nitrogen, leaving a yellow crystalline salt. M. Lefort states that this latter is a protonitrite of mercury; I find, on the contrary, that it is a subnitrate of the protoperoxide of mercury; in fact, it does not liberate any vapours of hyponitric acid in contact with sulphuric acid, and it yields with hydrochloric acid a mixture of the protochloride and of the perchloride of mercury. It is evidently the salt already obtained by Mr. Brooks under other circumstances, and to which that chemist has assigned the formula $Hg^2\ O, NO^5, 2HgO$. The metamorphosis giving rise to this subnitrate is well accounted for by the following equations:—

$$2(NO^5\ Hg^2\ O, 2HO) = NO^4 + (NO^5\ Hg^2\ O, 2HgO) + 4HO;$$

$$3NO^4 + 2HO = 2NO^5\ HO + NO^2.$$

It will be seen from the preceding that the composition of the nitrates of mercury is extremely simple, and is derived from a single type of combination, NO^5, MO + 2MO. In the neutral salt, 2MO is represented by water, which is removed *in vacuo*; in the subsalts, 2MO is represented by an oxide or by a hydrate; but in the latter case the water of the hydrate cannot be expelled without causing the total destruction of the nitrate.—*Comptes Rendus*, April 10, p. 432.

Observations on Chromium. By A. Moberg.

Berzelius found the equivalent of chromium to be 351·89. In the year 1844 this number was pronounced by Peligot to be inaccurate, because in the analysis of the acetate of the protoxide and of the perchloride of chromium he obtained smaller quantities of chromium than the calculation according to Berzelius's equivalent required. Peligot's determinations, however, left the atomic weight fluctuating between 325 and 330. At a subsequent period Berlin fixed it at 328·389.

Moberg has since employed the sulphate of the oxide of chromium and the sulphate of the oxide of chromium and ammonia, both of which leave on ignition oxide of chromium, in order to determine afresh the equivalent of this metal. The sulphate of the oxide of chromium was prepared according to Schrœtter's method, by boiling hydrated oxide of chromium with sulphuric acid; the former was precipitated from a solution of pure chrome alum by ammonia, then dissolved in muriatic acid, and again precipitated with ammonia. However, the results obtained with this salt were not sufficiently accurate. It retained a small quantity of sulphuric acid, which could be expelled by heating the salt up to 626° F. without the salt being decomposed. All the sulphuric acid could be subsequently expelled by a strong red heat. The atomic weight of chromium, determined in this manner, amounted to 332·538, 332·599, 333·313.

In a second series of experiments, the sulphate of chromium, as it will bear a faint red heat without decomposition, was first heated to a dull red, in order to free it from adherent sulphuric acid; in this state the salt, when subsequently exposed to an intense red heat, experienced such a loss in weight as made the atomic weight of chromium amount to 336·371, 336·019.

The numbers resulting from these determinations leave the question in considerable doubt, owing to the uncertainty of the method. The following experiments were therefore made with the sulphate of the oxide of chromium and ammonia, which was prepared partly from chromate of lead with sulphuric acid and alcohol, and neutralizing the liquid with ammonia, and partly by dissolving hydrated oxide of chromium in sulphuric acid and the addition of ammonia. The salt was reduced to a powder, and then dried for a considerable time under a bell-glass upon blotting-paper, at about 64°, upon which it was weighed in a platinum crucible and heated to red-

ness. The numbers obtained in this manner are 334·332, 334·207, 334·206, 334·769, 335·980, 334·945, 335·601, 335·012, 334·278, 335·372, the average of which is 334·870.

*Protoxide of Chromium**.—Moberg is of opinion that those chromiferous minerals which do not exhibit the peculiar colour of the oxide of chromium, as for instance chrome-iron ore and pyrop, contain protoxide of chromium. According to the formula of chrome-iron $(FeO, MgO) + (Cr^2O^3, Al^2O^3)$, the oxygen of the electro-negative constituents should be three times as great as that of the positive, which however is not the case in the analyses of Berthier, Laugier, Seybert and Abich. The author analysed the black shining chrome-iron ore of Beresow, which is scarcely magnetic, and found, when the constituents of the above formula were supposed to correspond to RO, R^2O^3,—

		Oxygen.	
Oxide of chromium	64·17	19·84	
Alumina	10·83	5·06	25·37
Silica	0·91	0·47	
Protoxide of iron	18·42	0·49	
Magnesia	6·68	2·59	6·68

Hence, even when the small quantity of silicic acid is neglected, so considerable an excess of electro-negative constituents results, that it must undoubtedly be admitted that a portion of the chromium is contained in the chrome-iron ore in the state of protoxide. It is probable that the chrome-iron ore consists of protoperoxide of chromium, protoxide of iron and oxide of chromium, protoperoxide of iron, oxide of chromium and magnesia, alumina and magnesia. Upon this supposition the following formula may be advanced for chrome-iron ore, which satisfies the condition required by the formula RO, R^2O^3, that the amount of oxygen of the negative bodies is three times as great as that of the positive:—

		Oxygen.	
Oxide of chromium	58·40	18·06	
Alumina	10·83	5·06	23·59
Silica	0·91	0·47	
Protoxide of chromium	5·17	1·18	
Protoxide of iron	18·42	4·09	7·86
Magnesia	6·68	2·59	

Ignited in a current of hydrogen, the chrome-iron ore experienced a slight reduction, which extended probably to the protoperoxide of iron.

The behaviour of pyrop towards acids, and likewise its colour, render it not improbable that the chromium which it contains is in the state of protoxide. An analysis, which the author made, of the transparent red granules of Bohemian pyrop, afforded, on calculating the chromium as protoxide,—

* The author observes, that he published the discovery of the protoxide of chromium before the Finland Academy of Sciences on the 1st of April 1844, much earlier therefore than Peligot, Oct. 12, 1844.

		Oxygen.	
Silica	41·353	21·483	
Alumina	22·353	10·440	
Protoxide of iron	9·941	2·291	11·15
Lime	5·294	1·513	
Magnesia	15·000	5·806	
Protoxide of chromium	4·176	0·960	
Protoxide of manganese	2·588	0·580	

Hydrated Protoxide of Chromium.—Protochloride of chromium, as obtained by the reduction of the perchloride in a current of hydrogen, mixed perhaps with some metallic chromium, deposits, on the addition of potash to its solution in water which has been well boiled, and from which the oxygen of the atmosphere is perfectly excluded, a yellow precipitate of hydrated protoxide of chromium. It was washed with water, which had been previously well boiled, in an apparatus which prevented the access of atmospheric oxygen, and then dried in a current of hydrogen. In the dry state it had a brown colour, which appeared dirty from the admixture of a trace of oxide; it was insoluble in dilute, and slowly soluble in concentrated acids upon the application of heat; it was preserved for three years unaltered in dry air. The analysis of this hydrated protoxide led to the composition CrO + HO, or 79·46 protoxide of chromium and 20·54 water. On ignition, the hydrogen of the water is set free, while the oxygen combines with the protoxide to form oxide. This brown hydrated protoxide is distinct from the brown precipitate obtained by Peligot from the protochloride of chromium by potash. Peligot excluded the access of air in an imperfect manner, and the body obtained by him is $CrO, Cr^2 O^3, HO$.—*Journ. für Prakt. Chem.*, xliii. p. 114.

On the Liquid Chloride of Selenium. By M. Sacc.

In seeking to determine the equivalent of selenium from the protochloride, I found by synthesis, weighing the chlorine absorbed by a certain weight of selenium, the numbers 547·20, 513·04, 499·31, 488·96; and by the determination of the chlorine with nitrate of silver, the numbers 599·50, 563·36, 540·12, 517·66. These determinations having been made with every possible precaution, and the error accompanying them being always in the same direction, it must arise from one and the same cause, which can be nothing else than the presence of some liquid chloride in the protochloride analysed, in which it is easily detected from the more or less yellow tint it communicates to this compound, which when pure is perfectly white.

To prepare this chloride, a slow current of dry chlorine was passed through a long glass tube, filled with fragments of pure selenium in a melted state, strongly inclined on the opposite side to that on which the chlorine arrived; the action soon commenced, and the heat produced by the union of the chlorine with the selenium volatilized the compound, which condensed in the cold parts of the tube, and was

collected in a well-dried phial. This compound is excessively volatile, and has a penetrating odour, calling to mind that of hydrofluoric acid; it is of a very deep orange-brown colour, not very fluid; and moistens glass just like oil. When thrown into cold water, it becomes coated with a red efflorescence, beneath which it preserves its fluidity for several days; in boiling water it appears to become immediately solid, passing wholly into the state of insoluble selenium on the one hand, and into hydrochloric acid and selenious acid on the other; but this is not exactly the case, for in the four analyses the supposed selenium was always found to disengage, when dried at 212°, hydrochloric and selenious acids, derived from the reciprocal reaction of the water and of the undecomposed liquid chloride, which it contains without doubt mechanically. To analyse this chloride, it was heated in one case with water at 212°, to determine the amount of selenium which then separates, and in the other treated directly with bisulphite of ammonia and an acid, neglecting the chlorine, the amount of which had to be determined by the loss, there being no method of separating it entirely from selenium.

I. 0·9963 grm. of the chloride afforded with water 0·2955 selenium; then with the nitrate of silver, 2·4888 chloride of silver; and lastly, 0·3783 selenium.

II. 2·3420 of chloride afforded, under the same circumstances, 0·6873 selenium and 6·0850 chloride of silver; an accident prevented the amount of selenium remaining in solution from being determined.

In the calculation of these two analyses, only the amount of selenium which separates by contact with water can be taken into consideration; for the solution not having been acidified before determining the chlorine, for fear of altering the condition of the substance, so great an amount of selenite was precipitated with the chloride of silver, that this determination and that which succeeded were rendered altogether erroneous. These two analyses represent in 100 parts—

	I.	II.	Mean.
Selenium precipitated by water..	29·6597	29·3467	29·5032

To complete this analysis, the whole of the selenium existing in the chloride was determined by pouring it into a cold solution of bisulphite of ammonia, which is subsequently heated, and the selenium then precipitated with an excess of hydrochloric acid. The precipitate, collected upon a weighed filter, was washed with the greatest care, then dried at 212°; but whatever care was taken, the paper always became friable, and during the desiccation hydrochloric and selenious acids were disengaged, arising from the decomposition pointed out above. One of the precipitates, which was dried in a porcelain crucible, showed upon the margin of the filter some minute acicular crystals, which proved to be selenious acid. The other precipitate, dried in a silver crucible, offered nothing similar; but the outer sides of the crucible became very black, and a thin pellicle of a brilliant black colour separated, which analysis proved to be seleniuret of silver, the properties of which correspond in every respect with that of the sulphuret of the same metal. The increase in weight of the

crucible, owing to this absorption of selenium, admits of adding to the precipitate the quantity of this metalloid, which having separated undoubtedly in the state of selenious acid, as in the first instance, had been reduced by the silver.

The selenium obtained had a very peculiar grayish appearance; it was perforated with small cavities like a scoria; when heated in a tube closed at one end it melted, disengaging a perceptible quantity of pure selenious acid, the formation of which must have necessarily increased the weight of the selenium, as is proved by the calculation of the two analyses.

III. 0·8930 grm. of the chloride gave, on treatment with bisulphite of ammonia and hydrochloric acid, 0·6426 selenium, which was combined with 0·2504 chlorine, determined by the loss.

IV. 2·92 grms. of chloride gave, under the same circumstances, 2·0994 selenium, combined with 0·8206 chlorine, estimated by the difference. This gives in 100 parts—

	III.	IV.	Mean.
Selenium	71·9597	71·8973	71·9285
Chlorine.....	28·0403	28·1027	28·0715

These analyses lead exactly to the formula $Cl^2 Se^5$, which cannot be admitted, both because it fails to explain the mode of decomposition of the chloride in the presence of water, and especially because it rests upon a faulty determination, the weight of the selenium being too high by the whole quantity of selenious acid which accompanies it; and, on the contrary, the chlorine of the compound, having been determined by the difference, is too low precisely by this quantity. This has led me to adopt Berzelius's formula, $Cl\,Se^2$, for the liquid chloride, which, calculated with Se = 490·93 and Cl = 443·20, gives the following composition in 100 parts:—

Selenium.....	68·89
Chlorine	31·11

According to this formula, the chloride should yield to water 34·44 per cent. of selenium, while only 29·50 were found; the loss must be solely attributed to the proportion of chloride retained by the selenium, and which is far more considerable in that precipitated by water than in that obtained by the bisulphite of ammonia; in fact, it disengages a perceptible quantity when heated in a test-tube before being dried in the water-bath. The formula $Cl\,Se^2$ explains all the reactions presented by the analysis of this compound, which establishes a further analogy between selenium and sulphur.

When the chloride of selenium is decomposed in the presence of water, it appears to resolve itself directly into selenium, hydrochloric and selenious acids, although the quantity of oxygen is twice that of the chlorine existing in the chloride; at least the solution obtained after the reaction exhibits all the distinctive characters of selenious acid, so that the formula of this reaction should be $ClSe^2 + 2HO = ClH, SeO^2, Se, H$.

Whether the gas which is always disengaged in this reaction is really hydrogen could not be ascertained, owing to its small quantity.—*Ann. de Chim. et de Phys.*, May 1848, p. 124.

On a cheap Method of preparing Oxide of Antimony. *By* E. G. Hornung.

M. Frederking having published a process for the preparation of the oxide of antimony by means of sulphuric acid*, I have made some experiments to ascertain whether the same process would not succeed on substituting the sulphuret of antimony for the metal. I mixed in an iron caldron 15 parts of sulphuret of antimony in the state of a very *fine powder* with 36 parts of sulphuric acid, and left the whole for the night exposed to a gentle heat. The mixture first thickened, and subsequently became again liquid when the temperature was raised and it was frequently agitated. At last the mass became whitish, some sulphur fused and separated, and a large quantity of sulphurous acid was disengaged; I continued to heat the mixture, stirring it constantly, as long as any disengagement of sulphurous acid and combustion of sulphur was observed. When the vapour consisted only of sulphuric acid, I added water gradually to it, and washed the mass to remove the free sulphuric acid. I then decomposed the subsulphate of antimony with carbonate of soda, and washed the oxide of antimony obtained; 15 parts of the sulphuret of antimony furnished 13 parts of dry oxide of a greenish-white colour, which, with the exception of some slight impurities, dissolved in tartaric acid. This process is the most œconomical for the preparation of the oxide destined to be converted into tartar-emetic.—*Journ. de Pharm.*, May 1848.

Researches on the Combinations of Silicium. *By* I. Pierre.

Doubts are still entertained as to the formula which should be assigned to silicic acid, and consequently to the chloride of silicium. Some chemists admit that silicic acid should be represented by the formula SiO^3, and adopt the number 266·82 as the equivalent of silicium; others prefer the formula SiO^2, taking $Si = 177·88$. Lastly, some are of opinion that the rational formula of silicic acid is SiO, and the equivalent of silicium 88·94.

The first of these formulæ, admitted by the majority of mineralogists, has the imposing authority of Berzelius, Thenard, &c. The formula SiO^2, adopted by a certain number of German chemists and mineralogists, among whom may be mentioned M. Gmelin, possesses the advantage, according to M. Cahours, of making the volume of vapour representing the equivalent of the protosilicate of ethyle of M. Ebelmen enter within the ordinary conditions. Lastly, the formula SiO seems at present to be generally admitted by the majority of French chemists; it was proposed long since by M. Dumas, when he published his beautiful investigation upon the specific gravities of vapours. M. Ebelmen, in his interesting memoir upon silicic æthers, has adopted this latter opinion after a very learned and profound discussion.

* Chem. Gaz., vol. ii. p. 499.

As the curious facts of the ætherification of silicic acid do not appear to have resolved the question completely in the eyes of a certain number of chemists, I proposed in the present investigation to ascertain whether it might not be possible to obtain, either by some facts of substitution or by the production of some double chlorides analogous to the double fluorides already known, or lastly, by the production of some new æther or amidogen compounds, results of such a nature as would allow chemists to base their selection upon more explicit and varied data.

The difficulties encountered in the preparation of the majority of these various kinds of compounds, the long and tedious manipulations required by researches of this class, in which the chloride of silicium is the first indispensable material,—all these circumstances combined did not admit of my varying and multiplying the operations to the extent I desired; but imperfect and incomplete as they are, I think they deserve to fix for a moment the attention of chemists.

I. *Compounds derived by Substitution from the Chloride of Silicium.*—The facts exposed in this first part of my investigation may be resumed in the following propositions:—

1. The chloride of silicium may be deprived, at a high temperature, by the action of hydrosulphuric acid, of the whole of its chlorine, and the latter replaced by an equivalent quantity of sulphur, passing through a series of intermediate compounds containing silicium, chlorine and sulphur.

2. The first of these intermediate compounds, the body $SiSCl^2$, is readily isolated on account of its great stability.

3. The sulphuret of silicium may likewise be obtained perfectly pure.

4. The existence of the compound SiS^2Cl is rendered highly probable from certain reactions which take place between alcohol or wood-spirit and the intermediate chlorosulphuretted products.

In concluding this short notice, it may perhaps not be uninteresting to arrange in a comparative table the expressions representing these different compounds, according to each of the three views of the molecular constitution of the chloride of silicium:

	Si = 266·82.	Si = 177·88.	Si = 88·94.
Chloride of silicium....	$SiCl^3$	$SiCl^2$	$SiCl$
Chlorosulphuret	$SiSCl^2$	$Si^3S^2Cl^4$	Si^3SCl^2
Chlorobisulphuret	SiS^2Cl?	$Si^3S^4Cl^2$?	Si^3S^2Cl?
Sulphuret.....	SiS^3	SiS^2	SiS

If regularity and simplicity deserve to be taken into consideration, the preference will undoubtedly be given to the first series with Si = 266·82.—*Comptes Rendus*, May 15, 1848.

On some double Chromates. *By* Dr. E. Schweitzer.

Chromate of Potash and Magnesia is obtained by adding *magnesia alba* to a moderately concentrated solution of bichromate of potash, heating and evaporating to crystallization. It forms beautiful

yellow crystals, belonging to the hemi-prismatic system. Its formula is

$$2CrO^3, KO, MgO + 2\,aq.$$

When heated, it acquires an orange colour, melts at an incipient red heat, disengages oxygen, and leaves a mixture of magnesia and a compound of oxide of chromium and magnesia; the latter is of a beautiful brown colour, insoluble in alkalies and acids, and is represented by the formula $MgO + Cr^2 O^3$.

Chromate of Potash and Lime.—When prepared in an analogous manner to the above, it is decomposed on evaporating the liquid; it is best to saturate the bichromate of potash with hydrate of lime, to pass a current of carbonic acid into it, and to concentrate the solution at a temperature between 86° and 104° F. It forms silky acicular crystals of a lemon colour. Its formula is $2CrO^3, KO, CaO + 2\,aq.$ It melts at a red heat without decomposition.—*Journ. für Prakt. Chem.*, xxxix. p. 297.

On the Train Oil of Balæna rostrata, *the Beaked Whale.* *By* E. A. Scharling.

This oil, which has for some time formed an article of commerce in Norway, Sweden and Denmark, becomes turbid at 46° F., and forms a paste a few degrees above 32° from the large amount of crystals which separate. It is far better suited for purposes of illumination in lamps than the ordinary train oil. A sample first sent to the author was nearly colourless, and had a very disagreeable odour, which however was easily removed; other samples, subsequently received, were of a dark colour, and had likewise a disagreeable odour. The author ascribes both these properties to the circumstance that the oil was sent in dirty vessels. But what most characterizes this oil is its highly illuminating power; it burns with a brighter flame than the ordinary train oil; the intensities of the light of two Argand lamps, of which the one was filled with ordinary train oil and the other with train oil from the beaked whale, were as 1 : 1·57. The flame of the latter smoked much less than that of the former, and the amount of oil consumed in an hour was less than that of the ordinary train oil required to produce the same effect. The low specific gravity = 0·8807 at 52° allows of its purity being tested by means of an ordinary alcoholometer. On exposing a quantity of this oil to a temperature of 17°, a solid mass of fat separated, which was collected on a filter, and submitted to pressure between paper. After frequently repeating this latter operation, it melted at 75°; it was a mixture of several fats, and contained a little spermaceti.

On boiling with commercial potash, a milky soap was obtained, which was separated with chloride of sodium and dissolved in alcohol. The salt which separated on cooling was agitated with æther to remove every trace of spermaceti, then dissolved in water, and precipitated with nitrate of silver. The silver salt assumed on drying

a somewhat dark colour, and left on ignition 38·90 silver = 41·78 per cent. oxide. The following results were obtained on the combustion of the silver salt:—

Carbon.....	42·82	20 =	1500·0	43·01
Hydrogen	6·93	19	237·5	6·82
Oxygen	8·47	3	300·0	8·62
Oxide of silver	41·78	1	1449·0	41·55

This solid fat occurred however in so small a quantity, that the author is inclined to believe that it is not peculiar to the oil, but an impurity.

In order to obtain the oil destined for the experiments perfectly pure, it was dissolved in boiling anhydrous alcohol, which dissolved half the weight of it. The oil which again separated on cooling was washed with water, then filtered through charcoal, and dried over chloride of calcium. After this treatment it is perfectly free from smell, and has a specific gravity at 56° of 0·873, at 66° of 0·8705, and at 68° of 0·868. Now since the specific gravity of the crude oil is likewise 0·868 at 68°, its constituents cannot have experienced any change by the above process of purification.

The purified oil yields, on dry distillation, but very small traces of compounds of acryle; not a trace of fixed ash nor of iodine was found in it. It is a very bad conductor of electricity; it absorbs oxygen from the air. When a current of air is passed through the oil for some time, it increases in specific gravity and becomes thick. A sample which had been exposed for six weeks to the air and sunlight had at 72° the specific gravity of 0·942. In small shallow vessels it becomes coated on the surface with a thin adherent pellicle, but the remainder dries up very slowly.

On dry distillation, a few dark drops first passed over, and then a colourless product; the gases which were evolved during the operation consisted of carbonic acid and hydrocarbons. Not a trace of sebacic acid nor of acryle compounds could be detected in the distillate.

The chief mass of the train oil of the beaked whale consists of a peculiar acid resembling oleic acid. On boiling with potash, the soap which is formed is turbid, probably owing to the presence of spermaceti. On boiling with milk of lime, a granular mass is formed, and in the supernatant water mere traces of glycerine were found.

To determine more closely the nature of the acids, the author adopted the following process:—The oil, mixed with finely-powdered litharge, was kept for ten hours at a temperature of 230°–266°, small quantities of water being added from time to time. When the saponification was complete, the lead plaster was repeatedly exhausted with boiling water, sulphuretted hydrogen passed through the filtered aqueous liquid, the sulphuret of lead separated by filtration, and the liquid itself evaporated to dryness. It left a small brown residue, in which the author was not able to determine any particular constituent with certainty.

The exhausted lead salt was now shaken with æther, when one

portion dissolved. The insoluble portion was decomposed with muriatic acid; the fatty mass thus separated was dissolved in alcohol of 0·826 specific gravity at 63°. On cooling with ice, a crystalline substance separated, which could be separated into two distinct fatty substances; on heating it to 120°, the greater portion of it melted, and this liquid portion poured off, possessed on cooling the properties of spermaceti. The remainder did not melt even at 212°; it puffed up, and appeared to be decomposed; it was not examined more minutely.

The soluble constituent of the lead plaster was decomposed with sulphuretted hydrogen after distilling off the æther. The acid thus separated was solid at a few degrees above 32°, and formed at 61° a perfectly transparent liquid. It had a yellow colour, and strongly reddened blue litmus-paper. On combustion it furnished the following results:—

Carbon	77·06	76·96	38 =	2850	77·03
Hydrogen	12·47	..	36	450	12·16
Oxygen	10·47	..	4	400	10·81

The following baryta salt was prepared according to the process described by Gottlieb in his examination of oleic acid. The acid, saturated with ammonia, was precipitated with chloride of barium; the washed salt was dissolved in hot alcohol of 0·842 spec. grav. On cooling, it separated in a crystalline state, and was purified by recrystallization. On desiccation at 212°, the salt did not melt; it caked somewhat together, and acquired a yellow colour. On analysis it furnished—

Carbon	63·01	62·71	62·42	38 =	2850·0	62·74
Hydrogen	9·62	9·59	9·68	35	437·5	9·61
Oxygen	6·17	6·50	6·70	3	300·0	6·63
Baryta	21·20	21·20	21·20	1	955·0	21·02

The æther was prepared by dissolving the acid in alcohol, and passing a current of dry muriatic gas through it; it separated as an oily liquid, which possessed a neutral reaction after it had been boiled with water. Dried over chloride of calcium, it furnished on analysis—

Carbon	77·75	77·25	42 =	3150	77·77
Hydrogen	12·56	12·85	40	500	12·34
Oxygen	9·69	9·90	4	400	9·89

On passing a current of nitrous acid into the oil, it becomes darker, and at last solid. After this solid mass has been exhausted with boiling water, it can be separated by means of alcohol into two substances, one of which is soluble, of a reddish-yellow colour, and liquid, whilst the other is colourless, solid, and very sparingly soluble in alcohol; the latter crystallizes from alcohol, and after frequent recrystallization dissolves in 10 parts of alcohol, and melts at 90°; the liquid substance remains in the mother-ley.

The products of distillation, which, as already stated above, consist chiefly of a colourless liquid, appear to be hydrocarbons with

one or more fatty acids, and probably mixed with a portion of unaltered oil. Some of the volatile fatty acids likewise occur, especially butyric acid. From a portion of the distillate, which was first digested with carbonate of soda, then washed with water, and again submitted to distillation in the water-bath, an oily liquid of a strong odour was obtained, which proved to be a mixture of several substances, which were not further separated.

On rectifying the distillate over potassium, a liquid was obtained which burnt with a very luminous flame and possessed an aromatic odour. The density of its vapour was found to be 5·81. Analysis gave 85·164 per cent. carbon and 14·510 hydrogen; according to which this liquid is a hydrocarbon of the formula $C^{12} H^{12}$, which is identical with that assigned by Gerhardt to the hydrocarbon which he obtained on the dry distillation of wax.

The train oil itself has the following composition:—

Carbon	79·89	80·01	79·648	79·923
Hydrogen	13·98	13·21	13·178	13·078
Oxygen	6·13	6·78	7·174	6·999

According to Smith's analysis, spermaceti consists of 80·18 carbon, 13·22 hydrogen, and 6·0 oxygen, which comes very close to that of the train oil under examination.

This train oil consists principally of a very liquid fat which contains no glycerine. The spermaceti contained in it amounts scarcely to 1 per cent.; the other fats which are found in it do not occur to a greater extent. The oil appears to be a compound of an acid with a base, which may be derived in the following manner from the above analyses of the acid and of the oil itself. Admitting the composition of the oil as required by analysis to be $C^{62} H^{60} O^4$, we have

New acid	$= C^{38} H^{35} O^3$
New base	$= C^{24} H^{25} O$
	$C^{62} H^{60} O^4$

Journ. für Prakt. Chem., vol. xliii. p. 257.

Observations on Manna. By J. Stettner.

The author gives the following account of the cultivation of the manna ash and the collection of the manna, from observations made in Sicily during the summer of 1847. The manna ash, *Fraxinus ornus*, in the manna districts of Capace, Cinesi and Fabarotto, where the best manna is obtained, does not form woods, as is generally supposed, but is cultivated in separate plantations. These plantations generally form regular squares, hedged in with *Cactus opuntia*. The trees are planted in rows, are from 2 to 8 inches in diameter, with stems from 10 to 25 feet high, which from the first shoot are kept smooth and clean. The soil is carefully loosened and kept free from weeds. After the eighth year the trees yield manna, which they then continue to do from ten to twelve years, when they are cut down and young shoots from the roots trained; one root-stock fre-

quently yields from six to eight new trees and more. For the production of the manna, young and strong shoots are requisite; but they are not tapped before the tree ceases to push forth any more leaves, and the sap consequently collects in the stem. This period is recognised by the cultivators from the appearance of the leaves; sometimes it occurs earlier than at others, and the collection of the manna takes place either at the beginning of July or only in August. Close to the soil cross sections are made in the stem, and in the lowermost sections small leaves are inserted, which conduct the sap into a receptacle formed by a cactus leaf; this is the way the manna *in sorte* is obtained. The incisions are repeated daily in dry weather, and the longer this continues the more manna is obtained. The stems are left uninjured on one side, so that the manna runs down the smooth bark more easily. The next year the uninjured side is cut. The *Manna cannelata* is obtained from the upper incisions, more than forty of which may be counted on one tree. The sap is there not so fat as below, and consequently dries more easily into tubes and flat pieces. After the manna has been removed from the trees. it has to be further dried upon shelves before being packed in cases, The masses left adhering to the stems after removing the inserted leaves are scraped off, and constitute the *Manna cannelata in fragmentis. Cannelata, Can. in fragm.* and *Capace* are collected at the same time from one stem—the more *Cannelata*, the younger, and the more *Capace* or *Gerace*, the older the stem. In Sicily the latter is designated *in sorte*, and is probably the most active. Dry and warm weather is essentially requisite for a good harvest.—*Archiv der Pharm.*, vol. liii. p. 194.

On some Salts of the Protoxide of Tin. By M. Bouquet.

Sulphate of the Protoxide of Tin, SnO, SO^3, is easily obtained by dissolving recently-precipitated protoxide of tin in warm dilute sulphuric acid. From the saturated solution nacreous laminæ separate, which are very soluble in cold water. The solution continues for a few minutes clear, but soon deposits a white basic salt. It forms double salts with sulphate of potash and sulphate of ammonia, which are not so readily decomposed.

Tartrate of the Protoxide of Tin is prepared by pouring a concentrated solution of protoxide of tin in acetic acid into a boiling solution of tartaric acid until the liquid begins to deposit crystals. It crystallizes in prisms with rectangular base, is soluble in cold, more readily so in hot water, and is not decomposed. It dissolves still more readily in tartaric acid, and no precipitate is produced in this solution by ammonia. Its formula is $C^8 H^4 O^{10}, 2SnO$. Crystalline double salts are formed when protoxide of tin is treated with bitartrate of potash or ammonia.

Oxalate of the Protoxide of Tin is obtained in a similar manner as the last salt; it is almost insoluble, and is deposited from the boiling liquid in shining needles. It is partially decomposed by boiling water, with deposition of a basic salt; its formula is $C^2 O^3 SnO$.

It dissolves in neutral oxalate of potash, soda or ammonia, with which it forms double salts.

Oxalate of the Protoxide of Tin and Potash is obtained by adding a considerable excess of the protoxide of tin to binoxalate of potash, in large colourless crystals. It dissolves easily in cold water; the solution, after a time, becomes milky; on boiling, decomposition rapidly ensues; sometimes a white gelatinous, sometimes a black precipitate being deposited. The formula of the crystals is

$$C^2 O^3 Sn O + C^2 O^3 KO + HO.$$

Oxalate of the Protoxide of Tin and Ammonia is isomorphous with the preceding salt.

Oxalate of the Protoxide of Tin and Soda is anhydrous and crystalline.—*Journ. de Pharm.*, xi. p. 460.

On the Action of Bromine upon the Citrates. By A. Cahours.

It is well known that most of the fixed ternary acids which yield pyrogenous acids have the property in common of being converted, by the action of hydrate of potash at about 380° F., into oxalic and acetic acids, on which account several chemists assume the existence of oxalic and acetic acids in these acids. With the view of solving this question, the author has examined the action of bromine upon several salts of these acids.

Action of Bromine on Oxalates.—When bromine is added in drops to a solution of oxalate of potash or soda containing a small excess of alkali, no reaction is perceptible until the temperature has risen to 104°–122°; pure carbonic acid is disengaged, and the solution contains bromide of potassium: $C^2 O^3, MO + Br = MBr + 2CO^2$.

Action of Bromine upon Acetates.—Upon the addition of bromine to solutions of acetate of potash or soda, no reaction occurs, but a large quantity of bromine is dissolved. The liquid is decolorized on spontaneous evaporation, but more quickly when heated. It leaves on evaporation a residue which is almost entirely soluble in alcohol; the alcoholic solution yields on evaporation pure acetate of potash.

Action of Bromine upon Citrate of Potash.—When bromine is added in small quantities to a concentrated solution of citrate of potash, the former disappears with evolution of heat and a violent effervescence, produced by the escape of pure carbonic acid. An excess of bromine is added, and then again carefully removed by dilute potash, when an oily, colourless, very heavy liquid is seen to subside. The most volatile substance contained in this oily liquid is bromoform; the least volatile is partially altered by heat, is solid, crystallizes, and is at all events a new substance. A third substance is formed, but in so small an amount that the author did not succeed in separating it from the two others.

The crude oil is washed with water and distilled with it as long as drops of oil pass over with the aqueous vapours. The distillate is freed from water by decantation, and then by chloride of calcium. The liquid thus purified is colourless, and of an agreeable aromatic

odour; its specific gravity is 2·9 at 54°, and its boiling-point 306°. A concentrated solution of potash decomposes it into formiate of potash and bromide of potassium. Analysis likewise gave the composition of bromoform, C^2HBr^3. The density of its vapour was found to be 8·63.

An oily substance, which crystallizes on cooling, remains in the retort beneath the water. It is washed with water, and dissolved in boiling alcohol, from which it separates on cooling in dazzling white, silky needles. This body also dissolves in æther and pyroligneous æther. It melts at 166°, and is partially altered on distillation with loss of bromine. A concentrated solution of potash dissolves it in the cold, and completely decomposes it on the application of heat; bromoform escapes, leaving behind bromide of potassium and oxalate of potash. Concentrated sulphuric acid dissolves little of it at a gentle heat; but on boiling, bromine escapes, and an oily body separates. When heated with nitric acid, a portion is dissolved, which separates on cooling in minute white needles. Analysis led to the formula $C^6 H Br^5 O^4$. The author calls it *bromoxaform*. Its formation is explained by the equation

$$C^{12} H^5 O^{11} + 5HO + 14Br = 6CO^2 + C^6 HBr^5 O^4 + 9BrH,$$

and its decomposition by potash by

$$C^6 HBr^5 O^4 + 4KO = 2(C^2 O^3, KO) + 2KBr + Cr^2 HBr^3.$$

It is probable that the bromoform which is found is first produced by the decomposition of this substance. The citrates of soda and baryta behave precisely like the potash salt towards bromine; the citrate of ammonia differs.

The examination of the products of decomposition of citric acid by heat by Dumas, and especially by Crasso, has shown that new compounds are formed, which stand in a simple relation to citric acid. When citric acid is carefully distilled, at first water passes over, and then a liquid of an aromatic odour, perfectly similar to that of acetone. It is collected in a fresh receiver until oily bands make their appearance in the neck of the retort. In this manner a pretty considerable quantity of a light mobile liquid is obtained. When some caustic potash is added to it, and then bromine in excess, a reddish-yellow heavy oil subsides, which possesses the properties and composition of bromoform. Cahours made the same experiment with acetone prepared from acetate of baryta, and likewise obtained a considerable quantity of bromoform.

When bromine is added in drops to a solution of itaconate or aconitate of potash, an increase of temperature is perceptible, and bubbles of gas are given off, which are coloured by bromine vapour. The gas obtained is carbonic acid. At first the solution of itaconate remains clear; but, on the further addition of bromine, it becomes turbid, and deposits an amount of an oily substance about equal in weight to the itaconic acid, which contains two different bodies; one forms about five-sixths of the whole, is acid, and yields crystalline salts with potash, soda and ammonia. The residue, insoluble in potash, resembles bromoform in odour, but differs from it in composi-

tion. The result is the same whether an itaconate or an aconitate is employed for these experiments; but, on the other hand, the products differ according to whether the alkali is in excess or not. If perfectly neutral aconitate of potash is dissolved in $1\frac{1}{2}$ part water, and bromine gradually added to it, the appearances above described are observed. The oily liquid is washed with water, then dissolved in very dilute potash, and the clear solution decanted from the residue mixed with dilute muriatic acid; this precipitates sometimes an oil, sometimes a substance of the consistence of butter, which subsequently becomes perfectly hard. Both bodies possess the same composition.

First Modification: *Liquid Acid.*—It is repeatedly washed with water until the latter no longer yields a precipitate with solution of silver when it is dried over sulphuric acid. It is then of an amber-colour, and possesses a faint peculiar odour, which on the application of heat becomes extremely irritating. It is heavier than water, very sparingly soluble in it, but dissolves in every proportion in alcohol and æther. It is partially destroyed by distillation; sometimes it remains fluid for months, and sometimes crystals form in it. Moderately-concentrated nitric acid scarcely attacks it in the cold; on boiling it, decomposition ensues; concentrated sulphuric acid dissolves it at a gentle heat, from which water again partially precipitates it. A concentrated solution of caustic potash evolves considerable heat when mixed with it, and disengages a peculiar odour. An oily substance is precipitated from the solution by acids. Analysis led to the formula $C^8\,H^6\,Br^2\,O^4$, which was confirmed by the analysis of the ammonia salt; the latter forms whitish-yellow scales, which are fatty to the touch and easily soluble in water and alcohol. Its formula is

$$C^{16}\,H^{15}\,Br^4\,NO^8 = 2C^8\,H^5\,Br^2\,O^3 + NH^4\,O + HO.$$

It is consequently an acid salt of ammonia.

When a solution of nitrate of silver is added to one of the above salt, a caseous precipitate is formed, which perceptibly dissolves in cold water; it easily cakes together, forming a pitchy mass; when quickly dried *in vacuo*, it forms a white powder, which gave on analysis 30·77 per cent. of silver; the formula $C^8\,H^5\,Br^2\,O^3$, AgO requires 30·60.

The formula of the acid was moreover confirmed by the analysis of the æther, which is somewhat difficult to prepare. The acid is dissolved in absolute alcohol, the solution kept at a temperature between 158° and 176°, and a current of dry muriatic gas passed through it. As soon as no more is absorbed, the acid liquid is distilled, a spirituous liquid passes over into the receiver, which is poured into water, when a heavy amber-coloured oil subsides, which is freed from muriatic acid and a small quantity of undecomposed acid by washing it with water containing soda, and then with pure water. The æther is dried *in vacuo* over sulphuric acid. It is liquid, almost colourless, heavier than water, in which it sparingly dissolves, whilst in alcohol it dissolves in every proportion. At the ordinary temperature its odour is very faint, but on warming it be-

comes penetrating, and causes tears to flow; its taste is biting, resembling horse-radish. It is partially decomposed on distillation. Analysis led to the formula

$$C^{12} H^{10} Br^2 O^4 = C^8 H^5 Br^2 O^3 + C^4 H^5 O.$$

The acid $C^8 H^6 Br^2 O^4$, which Cahours calls *bromotriconic acid*, probably originates from another $C^8 H^8 O^4$, which is isomeric with butyric acid. The author endeavoured in vain to prepare this substance by the action of bromine upon butyric acid or butyrate of potash, he therefore considers it probable that butyric acid is merely isomeric with it. On treating an alcoholic solution of the bromine compound with potassium-amalgam, according to the method described by Melsens for replacing chlorine or bromine by hydrogen, he obtained a precipitate of bromide of potassium; the alcohol contained a salt of potash in solution, from which acids precipitated a solid crystalline substance, which was easily soluble in water, especially on warming, and possessed the odour of the volatile fatty acids.

Second Modification: *Crystallized Acid.*—It was mentioned above that the acid liquid sometimes changed into a crystalline substance. It is also frequently obtained in this state when citrate of potash is treated with bromine, potash added to the crude oil, and after separating the neutral oil, the potash salt decomposed with dilute nitric acid. The crystalline flakes which separate are washed upon a filter with as little water as possible, as they are rather soluble in it; they are then dissolved in æther, from which, on spontaneous evaporation, the acid separates in long white needles. It melts at a low temperature, and on careful distillation may be almost entirely volatilized, leaving a mere trace of carbon. It is rather easily soluble in boiling water, from which it separates on cooling in minute silky needles; it dissolves readily in alcohol and æther. It furnishes soluble crystalline salts with potash, soda and ammonia, and gives sparingly soluble compounds with silver and lead. It disengages the same odour when heated with concentrated solution of caustic potash as the liquid acid. When an acid is added to the alkaline solution no precipitate is produced. Analysis led to the formula $C^8 H^6 Br^2 O^4$, according to which it possesses the same composition as the liquid acid.

The same phænomena occur when bromine is added to neutral itaconate of potash; the liquid acid formed had exactly the same composition as the preceding.

If aconitate of potash containing an excess of potash is employed instead of the neutral salt, an essentially different product is obtained from that above described. Carbonic acid is equally disengaged and a yellowish oil separates, the greater portion of which dissolves on the addition of potash, while an oily mobile liquid is left which possesses an agreeable aromatic odour. The alkaline liquid yields, on the addition of an acid, beautiful white crystalline flakes. To purify them they are washed with a little cold water, pressed and dried *in vacuo*. The acid separates from solution in æther on spontaneous

evaporation in long acicular crystals. It is colourless, soluble in every proportion in alcohol and æther, tolerably so in water, especially on boiling. When heated gently it is volatilized almost entirely without decomposition. Sulphuric acid, nitric acid and caustic potash behaved in the same manner towards it as towards the preceding. Analysis led to the formula $C^6 H^4 Br^2 O^4$, according to which it differs from the preceding acid by $C^2 H^2$. The author calls it *bromitonic acid.*

It has been observed that along with these acids another body is formed, which has an aromatic odour similar to bromoform; it is produced only in small quantity, and is very difficult to obtain pure, as it experiences partial decomposition by heat. After it has been repeatedly washed with alkaline water, and then with pure water, and dried over sulphuric acid *in vacuo*, it forms a tolerably mobile, very heavy liquid; it disengages hydrobromic acid when heated, and leaves a carbonaceous residue. It dissolves in every proportion in alcohol and æther. It furnished on analysis—

Carbon.....	11·71	11·81	11·41	6	12·20
Hydrogen	1·13	1·20	1·12	3	1·02
Bromine	82·93		83·85	3	82·71
Oxygen				2	4·07

Its equivalent could not be determined, as it does not enter into any combination, and is not volatile without decomposition. The action of bromine upon the alkaline aconitates may perhaps be explained by the following equation:—

$$2(C^{10} H^6 O^8) + 2HO + 10Br = 6CO^2 + C^8 H^6 Br^2 O^4 + C^6 H^3 Br^3 O^2 + 5BrH.$$

If instead of the neutral aconitate of potash a very alkaline salt is employed, another oil, insoluble in potash, which contains less carbon and more bromine than the preceding one, is obtained.

The alkaline salts of pyromucic and pyromeconic acids are isomeric with the anhydrous aconitic acid, and are violently attacked by bromine. A heavy reddish oil is produced, and at the same time the same penetrating smell which irritates the eyes so powerfully is evolved as in the case of aconitate of potash. The small quantities however of these acids did not permit of the products being submitted to more accurate examination.

It results from the preceding investigation that citric acid under the simultaneous action of alkalies and bromine gives rise to more simple compounds, which may be considered as produced by oxidation and subsequent substitution.

Tartrate of potash behaves in a very different manner to the citrate, only bromide of potassium and bitartrate of potash are formed; it is possible therefore by means of bromine to detect small quantities of citric in tartaric acid.

The alkaline tannates and gallates are violently attacked by bromine, a brownish resin being formed.—*Ann. de Chim. et de Phys.*, xix. p. 484.

Chromate of Potash and Deutoxide of Nitrogen.

According to Dr. Schweitzer, deutoxide of nitrogen is absorbed in considerable quantity by a solution of bichromate of potash; the liquid acquires a dark colour, and after some time a brown precipitate subsides, which after drying exhibits all the properties of the brown oxide of chromium, the chromate of the oxide of chromium (CrO^3, Cr^2O^3) of Maus, the peroxide of chromium (CrO^2) of Krüger.—*Journ. für Prakt. Chem.*, xxxix. p. 269.

On the Bark of Adansonia digitata *as an Antifebrile.* *By* Dr. P. Duchassaing.

The author, a physician at Guadaloupe, has employed the bark of *Adansonia* in intermittent fevers, the so-called marsh fever, with great success. It is very effective, may be had at little expense, possesses an agreeable taste, does not act upon the nervous system, and has a favourable influence upon digestion. In some cases this bark stopped the fever where the strongest doses of quinine had produced no effect. The decoction of the bark, which is obtained by boiling 1 oz. of the bark with a litre of water down to a third of this volume, generally suffices to cure this terrible fever. Adanson had observed this effect of the bark, as may be seen in his papers in the Memoirs of the French Academy. He writes that he used this bark to cure himself of the fevers of Senegal. The *Adansonia digitata* occurs in the greatest abundance in the French colony of Senegal, and may perhaps become a very important article of commerce. —*Comptes Rendus*, xxvi. p. 254.

On the Preparation of Schlippe's *Salt* (*Sulphantimoniuret of Sodium*). *By* M. Van den Corput.

This salt is prepared by conveying into a red-hot Hessian crucible an intimate mixture of the following substances reduced to a fine powder:—

Effloresced sulphate of soda	8 parts.
Sulphuret of antimony.....	6 ...
Vegetable charcoal	3 ...

The crucible is covered with a tile; when the fluid mass ceases to froth and the sulphate is considered sufficiently reduced, the contents of the crucible are boiled in a porcelain dish with 1 part of sulphur and a suitable quantity of distilled water. The filtered liquid is set aside to crystallize, and in the course of a short time furnishes colourless or slightly yellowish tetrahedra, of a biting saline taste, with a hepatic, metallic after-taste. This salt is insoluble in alcohol, but soluble in 3 parts of cold water. Its elementary composition is represented by the formula $3NaS + SbS^5 + 18HO$.—*Repert. der Pharm.*, March 1848.

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Observations on Aqua-regia. *By* M. Gay-Lussac.

In the opinion which has hitherto prevailed among chemists respecting the nature of *aqua-regia*, which is known to be a mixture of nitric and hydrochloric acids in variable proportions, it is admitted that the reaction between the two acids gives rise to chlorine and nitrous vapour, which, with the assistance of heat, are disengaged together until one of the acids is wholly exhausted. This is pretty nearly the opinion of Berthollet, which has now prevailed for more than sixty years, notwithstanding the important researches of Dr. E. Davy, published in 1830, and the still more recent ones of M. Baudrimont, made in 1843. The former chemist obtained, on treating ordinary salt with concentrated nitric acid, a peculiar gas mixed with chlorine, of a pale reddish-yellow colour, and which he found to be composed of equal volumes of chlorine and nitrous gas without condensation, although he did not succeed in separating it from the chlorine and obtaining it in a pure state. He likewise obtained the same gas, which he called chloronitrous gas, by mixing together chlorine and nitrous gas, an experiment previously made by Berthollet, who however did not examine the product.

These interesting results of Dr. E. Davy led M. Baudrimont to submit *aqua-regia* to further examination. Chloronitrous gas was prepared with a mixture of nitric and hydrochloric acids; and by conducting it into a tube immersed in a frigorific mixture of ice and salt, he condensed it into a dark brownish-red liquid, which boiled at about 7° C. below the temperature of melting ice. This important experiment, by furnishing the means of separating the new product from the chlorine which always accompanies it, enabled M. Baudrimont to submit it to analysis. He expresses its composition by the formula $NO^2 Cl^3$, which is that of nitric acid, NO^5, in which 3 equivs. of oxygen are replaced by 3 of chlorine. From this analogy of composition, it was called chloronitric acid; and as it was found to be very unstable, it was considered as the active principle of *aqua-regia*. But the composition $NO^2 Cl^3$, found by M. Baudrimont, does not explain the production of the chlorine which accompanies the chloronitric vapour; and it will subsequently be seen that it is indeed not accurate.

These researches of Davy and Baudrimont, although imperfect,

ought to have fixed the attention of chemists more seriously than they have done. Berzelius alone mentions them in the last edition of his 'Manual of Chemistry,' and even doubts the existence of the chloronitric acid of M. Baudrimont. He adheres to the received opinion, that the products of *aqua-regia* are chlorine and nitrous vapour.

In this obscure state of the question, I have made some experiments with a view to throw some light upon it; and I shall state in a few words the results at which I have arrived. The reaction between the elements of *aqua-regia* left to itself, and that which occurs in the presence of a metal or of any other body, must be distinguished. After mixing the nitric and hydrochloric acids, the reaction is soon manifested if the acids are very concentrated; but if dilute, it is necessary to raise the temperature. On passing the gaseous product into the frigorific mixture of ice and salt, the chloronitric vapour condenses, and is thus separated from the chlorine which accompanied it. The vapour of this liquid, passed into water, is instantly decomposed into hydrochloric and hyponitric acids, or into the products which result from the action exerted upon it by water. The chlorine is obtained by precipitating the solution with nitrate of silver; and if the chloronitric vapour is decomposed by mercury, the chlorine combines with the metal, leaving pure nitrous gas, the volume of which is very nearly equal to half that of the vapour employed. From the results obtained by analysis, chloronitric vapour may be represented by the formula $NO^2 Cl^2$, or by equal volumes of nitrous gas and chlorine. This vapour may consequently be considered as hyponitric acid, NO^4, in which 2 equivs. of oxygen have been replaced by 2 equivs. chlorine. The third equivalent of chlorine, due to the third equivalent of oxygen yielded by the nitric acid, is disengaged with the chloronitric vapour, mixed with it in the proportion of 1 to 4.

On receiving this mixture of chloronitric vapour and chlorine in water, the whole is absorbed, hydrochloric and nitric acids being reproduced, that is to say, a very dilute *aqua-regia*, which does not decolorize either the hypermanganate of potash or the sulphuric solution of indigo, whilst the solution of the vapour decolorizes the solution of the hypermanganate, owing to the hyponitric acid which it contains, and does not touch the indigo because it contains no free chlorine.

The preceding analysis, which led to the formula $NO^2 Cl^2$, must be considered to refer to a normal liquid; in fact, I obtained liquids which possessed this composition; but by varying the circumstances of production, others are obtained, which contain more nitrous gas. This will be better understood when it is known that another combination of nitrous gas and chlorine exists in which the latter gas is contained in less proportion than in the first liquid, and that both may be formed simultaneously.

This new compound is obtained by the direct mixture of the two gases; their combination is indicated by a brilliant orange colour, which the mixture assumes, and by a condensation which, compared

withthe real volume of the gases which have entered into combination, amounts exactly to one-third. The new compound remains gaseous at the ordinary temperature, but it condenses in the frigorific mixture of ice and salt to a liquid similar to that yielded by *aqua-regia*; the colour however is not quite so dark. It is likewise very volatile; but its boiling-point was not determined, because it was found that its composition, as in the case of the liquid $NO^2 Cl^2$, was not constant. Its analysis, deduced from the condensation which its two gaseous elements experience on rendering them alternately predominant in the mixture, leads rigorously to the combination of 2 vols. of nitrous gas to 1 vol. of chlorine, and consequently to the formula $NO^2 Cl$, analogous to NO^3, nitrous acid. But on analysing the liquid obtained by passing into the same receiver indeterminate currents of chlorine and nitrous gas, variable results are obtained, which approach more or less to the formula $NO^2 Cl$, which is obtained only by mixing the two gases in the exact proportion of 2 vols. of nitrous gas to 1 of chlorine.

It must consequently be admitted that the two compounds $NO^2 Cl^2$ and $NO^2 Cl$ nearly always accompany each other in variable proportions according to circumstances, and that in this respect they present the same capricious mobility as the hyponitric and nitrous acids, to which they may be justly compared; it is, in fact, only from the analogy of composition which exists between each of these two groups, that the term acid can be applied to the chlorinated compounds, for nothing hitherto proves that they possess this character.

On analysing by means of mercury the successive portions of vapour furnished by the same liquid derived either from the mixture of chlorine with nitrous gas, or from ordinary *aqua-regia*, or from a mixture of common salt and concentrated nitric acid, the quantity of nitrous gas constantly increases from the first portions to the last, which yield as much as 90- and 95-hundredths of their volume. It must thence be concluded, that the compound $NO^2 Cl^2$ is more volatile than $NO^2 Cl$; but it appears impossible to separate them accurately from their difference of volatility.

With reference to the two theoretical compounds $NO^2 Cl^2$ and $NO^2 Cl$, the calculated density of the vapour of the first is equal to 1·7402, and that of the second to 2·2594. The densities which were taken fell between these two limits; but on account of their variability, no greater attention was given to them.

Thus, from the reaction between the elements of *aqua-regia*, or from the union of the chlorine and nitrous gas, two products, $NO^2 Cl^2$ and $NO^2 Cl$, result in variable proportions according to circumstances. These products, which are accidental, and may be compared, as regards their production, to the nitrous vapour which concentrated nitric acid furnishes when exposed to the action of heat, are no more the essential principle of *aqua-regia* than is the nitrous vapour with respect to the nitric acid; and the most decisive proof of this may be given by causing the action of metals to intervene. Thus on treating leaf-gold with *aqua-regia*, the chloronitric vapour

is obtained at the same time with a solution of the gold, which is effected by means of the free chlorine accompanying the vapour. The solution of the gold is therefore perfectly independent of the production of the vapour, as it is effected in its presence and without its assistance. All those metals, as platinum, iridium, osmium, &c., which may be ranged in the same class as gold as regards their weak affinity for oxygen, are, like that metal, dissolved only by the liberated chlorine, and take no part in the formation of the chloronitric or chloronitrous vapour produced at the same time.

The case is different with respect to the other metals possessed of a stronger affinity for oxygen, on treating them with *aqua-regia*. If this is supposed to be already coloured by chlorine and by the chloronitric vapour which it holds in solution, the metal instantly renders it colourless by combining with the chlorine, which may be conceived to be in a free state, and with that of the chloronitric vapour which it decomposes. But, once deprived of this vapour, the *aqua-regia* furnishes no more, except perhaps at a distance from the surface of the metal, for it cannot be supposed that any can be formed in contact with the metal, in order to be decomposed by it at the same instant. The following reaction takes place between the *aqua-regia* and the metal. The nitric acid yields to the hydrogen of the hydrochloric acid all the oxygen which the metal might deprive it of to dissolve were it alone in contact with it, and in place of the oxygen the metal combines with the chlorine produced. Take copper for instance; on dissolving in nitric acid, nitrous gas is liberated, and consequently 3 equivs. of oxygen are furnished to it by the acid. But in presence of hydrochloric acid, the oxygen goes in preference to its hydrogen, and 3 equivs. of metallic chloride are obtained. The metals which do not decompose water, the protochloride of iron, phosphorus, arsenious acid, &c., furnish the same result when treated with *aqua-regia*, that is to say, only nitrous gas is disengaged. With the protochloride of tin, nitric acid parts with 4 equivs. of oxygen, and furnishes protoxide of nitrogen; the same gas is likewise produced with *aqua-regia*. With respect to the metals which decompose water, these, when treated with nitric acid, furnish ammonia, that is to say, the nitrogen loses the whole of its oxygen. Now these same metals, treated with *aqua-regia*, give the same result, 8 equivs. of tin for instance, when treated with a mixture of 1 equiv. of nitric acid and 9 of hydrochloric acid, dissolve with the assistance of heat without any perceptible disengagement of gas, and leave as residue the trace of arsenic which almost always accompanies this metal.

It may therefore be stated generally, that the gaseous products furnished by the metals with *aqua-regia*, excepting gold, platinum, &c. are precisely the same as they yield with nitric acid. With respect to gold, it is not attacked by nitric acid; and the gaseous products, chlorine and chloronitric vapour, which it furnishes with *aqua-regia*, are independent of its presence, and are determined solely by the reaction between the nitric and the hydrochloric acids.—*Comptes Rendus*, June 12, 1848.

Note on the Composition of Achmite. *By* EDWARD J. CHAPMAN*.

Achmite or acmite, a silicate occurring in a quartz vein in granite at Rundemyr near Kongsberg in Norway, was analysed, soon after its discovery in 1821, by Berzelius, and also by Stromeyer, with results from which the following formula was obtained, as exhibiting the most rational composition of the mineral:—

$$NaO, SiO^3 + Fe^2 O^3, 2SiO^3.$$

Since that time however the mineral has been examined by Von Kobell and other chemists, who have considered the iron to be in the state of protoxide, a belief which has gained the approval of most mineralogists, from the resemblance borne by the achmite to certain members of the pyroxenic group; and perhaps also from the dark colour and opacity of the mineral—characters more usually belonging to silicates of FeO than to those having the peroxide of iron for their base. On these grounds Frankenheim has not hesitated to assign to the achmite the accompanying formula, or that of an augite in which soda replaces a portion of the usual bases containing 1 atom of oxygen:—

$$3\left\{\begin{matrix}FeO\\NaO\end{matrix}\right\} + 2SiO^3, \text{ or } \left.\begin{matrix}Fe\\Na\end{matrix}\right\} S^2.$$

Now the achmite not being decomposed by acids without previous fusion with an alkaline carbonate, the iron in the subsequent treatment, even with hydrochloric acid, is necessarily met with in the state of peroxide, whether it originally existed in the mineral in that condition or not; and this being the case, a certain field is left open for speculation upon the disputed point. Looking at the circumstance that neither the analysis of Berzelius nor that of Stromeyer gives an excess in the total weight, and this with upwards of 30 per cent. of oxide of iron in the mineral, the older way of thinking would appear to be the true one. This I have been able to confirm by the method lately made known by me* of distinguishing the protoxide of iron from the peroxide by the blowpipe, a method particularly applicable in the examination of ferruginous silicates insoluble in hydrochloric acid. The achmite, in fact, added to a bead of borax in which oxide of copper has been dissolved, does not occasion the least reduction of the CuO to $Cu^2 O$, whereas this reduction is instantly effected by the addition of a small fragment of hornblende or augite to the same bead. At the same time the achmite is even more easily soluble in the borax glass than either of these minerals, so that its negative action can only arise from the absence of FeO. I should here, however, state that I have found certain hemitrope crystals of hornblende (the variety usually termed "basaltic hornblende") of a dark brown colour, as well as several opake crystals of augite, to contain peroxide of iron and to be entirely free from protoxide, a fact which I mention more especially, as I am not aware that it has been previously noticed; and, on the other hand, I have

* Communicated by the Author.

† See the Chem. Gaz., page 106 of the present volume.

discovered the presence of FeO in translucent crystals of staurolite, a mineral hitherto supposed to be a basic silicate of alumina in which a portion of the Al^2O^3 was replaced by Fe^2O^3; but on this subject I shall have more to add in a future paper.

If we regard the mineralogical formula of the achmite as being $NaS^3 + 3FeS^2$ according to the analysis of Berzelius, the mineral may be arranged in the classification of the silicates with the oligoclase or natron-spodumene, a substance possessing exactly the same kind of composition ($NaS^3 + 3AlS^2$), but with alumina in place of peroxide of iron. Notwithstanding, however, the isomorphous conditions of these oxides, the minerals themselves are not isomorphous, the achmite crystallizing in the monoclinic and the oligoclase in the triclinic system.

On the Constitution of Glycerine and the Oily Acids.
By Prof. James C. Booth.

When most of the fats are acted upon by an alkali or acid, they are divided into an acid and a body called glycerine. When glycerine is distilled, or any fat containing glycerine, a peculiar body, acroleine, is produced.

Acroleine.—The formation of acroleine by the distillation of glycerine, the oxidation of the former to an acid resembling the acetic and other reactions, evidently point out the relation of these bodies to an alcohol; a conclusion which has been drawn by several chemists. On the other hand, when we examine the composition of four alcohols,—methylic, $C^2H^4O^2$; æthylic, $C^4H^6O^2$; amylic, $C^{10}H^{12}O^2$; cetylic, $C^{32}H^{34}O^2$, all having the empirical general formula $C^nH^{n+2}O^2$, and compare this with the general formula of acroleine, $C^nH^{n-2}O^2$, or of glycerine, $C^nH^{n+2}O^6$, we observe a discrepancy which precludes us from classing either of the last with alcohol. Acroleine, as is well known, is obtained by the dry distillation of glycerine, or of any glyceric fat alone, or better by the distillation of glycerine with dry phosphoric acid. Its formula, deduced from its analysis, is $C^6H^4O^2$. By oxidation with nitric acid, acetic and formic acids are produced by the addition of 2 equivs. water and 4 equivs. oxygen; thus

$$C^6H^4O^2 + 2HO + O^4 = C^6H^6O^8 = C^4H^4O^4 \text{ (acetic)} + C^2H^2O^4 \text{ (formic)}.$$

By slower oxidation in the air, or by oxide of silver, which becomes reduced, it is converted into acrylic acid, $C^6H^4O^4$, which closely resembles acetic and formic acids both alone and in its salts. By slower oxidation in close vessels, acetic, formic or acrylic acid will result, while there is also formed disacrone; and Berzelius observes, that if we abstract C^2H from 2 equivs. acroleine, there remains disacrone, $C^{12}H^8O^4 - C^2H = C^{10}H^7O^4$; in which case the C^2H may be oxidized into acetic, formic or acrylic acid. Acrylic acid readily passes into acetic by the assumption of water, thus

$$2(C^6H^4O^4) + 4HO = 3(C^4H^4O^4).$$

When acroleine is decomposed by potash, it is first resolved into acrylate, and then into acetate and formiate of potash.

We might infer from these reactions that acroleine is either a conjugate acetic acid, of which the conjugate is

$$C^8 H^4, (C^{12} H^8 O^4 = C^8 H^4 + C^4 H^4 O^4);$$

or it is a conjugate formic aldehyde with the same conjugate,

$$C^4 H^2; (C^6 H^4 O^2 = C^4 H^2 + C^2 H^2 O^2).$$

But since it exhibits no properties of an acid, the latter is the more correct inference. Moreover, its behaviour to nitrate of silver strengthens this view; and its classification with aldehyde, by reason of its analogous behaviour, has already received notice from Berzelius and others. If acroleine be mingled with a solution of nitrate of silver, a white caseous precipitate appears, and the odour of acroleine disappears. After some moments, especially by the aid of warmth, the precipitate blackens, and acrylate of silver dissolves. Since the white precipitate cannot be a compound of acroleine and oxide of silver, the inference of Berzelius is that it is hypacrylite or acrylite of silver. The latter is most probable, and confirms the analogy between acroleine and aldehyde. This acrylous acid would be $C^6 H^4 O^3$. The formation of disacrone and disacrone-resin by keeping acroleine and the production of acrole-resin by an alkali tend to complete the analogy between aldehyde and acroleine. The rational formula for acroleine would therefore be $C^4 H^2$, $C^2 H^2 O^2$, or a conjugate methaldehyde (formic aldehyde).

On this view the several decompositions and changes of acroleine are more satisfactorily explained. Like aldehyde it is readily converted by slow oxidation into acrylous acid, and by stronger oxidation into acrylic acid, which is formic acid with the same conjugate, $C^6 H^4 O^4 = C^4 H^2$, $C^2 H^2 O^4$. By a still stronger oxidation the action does not stop here, but the conjugate participates in it, assuming 2 equivs. oxygen and 2 equivs. water, so that it becomes a mixture of acetic and formic acids, a successive change which is proved by the action of potash upon acroleine.

We are acquainted with methaldehyde in another combination, the formo-methylal. When oil of vitriol and methylic alcohol are distilled, mether or oxide of methyle is obtained; but when the acid is dilute and oxide of manganese is added, oxidation takes place, and formomethylal results, of the composition $C^6 H^8 O^4$. From its behaviour it is supposed to contain 2 equivs. mether and 1 equiv. hydrated oxide of formyle or methaldehyde,

$$C^6 H^8 O^4 = 2(C^2 H^3 O) + C^2 H^2 O^2 \text{ (\textit{Malaguti})}.$$

The former, mether, is formed by the separation of water; the latter by a slight oxidation of the mether. Where the oxidation is stronger, formic mether results from the oxidation of the formic aldehyde. Moreover, lignone or xylite appears to contain methaldehyde. Although we are not acquainted with the aldehyde of the formic series alone, yet we can thus trace it in combination or with a conjugate; and in the latter case we can trace it through a formous acid (acrylous) to a formic (acrylic) acid.

If we pursue the subject further, we might regard acetone (mesitic alcohol) as acrylic alcohol, and the oxide of mesityle or metacetone as acrylic æther, if they be found to produce acrylic acid, as alcohol produces acetic acid. The whole series may be thus represented:—

Metacetone	$C^6 H^5 O = C^4 H^2, C^2 H^3 O$
Acetone	$C^6 H^6 O^2 = C^4 H^2, C^2 H^3 O, HO$
Acroleine	$C^6 H^4 O^2 = C^4 H^2, C^2 H^2 O^2$
Acrylous acid	$C^6 H^4 O^3 = C^4 H^2, C^2 H O^2, HO$
Acrylic acid	$C^6 H^4 O^4 = C^4 H^2, C^2 H O^3, HO$

Glycerine.—The composition of glycerine is $C^6 H^8 O^6$; in combination with sulphuric acid, $C^6 H^7 O^5$; in combination with the fat acids, $C^6 H^6 O^4$ or $C^3 H^3 O^2$. In some it appears to be $C^3 H^2 O$, as in anamirtine, palmitine and laurine. The last is assumed by Berzelius to be the real base, and called by him oxide of lipyle. Admitting it to be the anhydrous base in the fats, it appears to be hydrated in some of them, $C^3 H^2 O, HO$ or $C^3 H^3 O^2$, and this hydrate in others to be doubled, $C^6 H^6 O^4$. The difficulty of recombining it directly with the fat acids points to a firm union of part of the water with the base, so that we may regard the separated glycerine as different from the combined base. By distillation alone, or with phosphoric acid, glycerine loses 4 equivs. water, becoming acroleine, $C^6 H^4 O^2$, and which I have shown to be formic aldehyde with the conjunct $C^4 H^2$. When distilled with butyric and sulphuric acids, water is also abstracted, the base of fats produced, and butyrine regenerated. When glycerine is exposed with yeast and water to a temperature of 68° to 86°, it is converted into acetonic acid of the formula $C^6 H^6 O^4$, so that the resulting change consists in the separation of 2 equivs. water. As it will be shown below that acetonic acid is formic acid with the conjugate $2C^2 H^2$, we may infer that the base of fats contains the conjugate $C^2 H^2$, making its rational formula $C^2 H^2, CO$. By the assumption of 1 equiv. water by 2 equivs. of the base, 1 equiv. dry acetonic acid results, $2(C^2 H^2, CO) + HO = C^6 H^5 O^3$. By the combustion of one-half of the hydrogen in the conjugate $C^4 H^4$, it is reduced to $C^4 H^2$, which is the conjugate in acroleine; whence we may infer that glycerine by distillation first loses 2 equivs. water as such, leaving $C^6 H^6 O^4$ or $C^4 H^4, C^2 H^2 O^4$, which last body is not formic acid, although isomeric with it. By the further action of heat, 2 equivs. of oxygen in the last body abstract 2 equivs. hydrogen from the conjugate, forming $C^4 H^2, C^2 H^2 O^2 + 2HO$, the two former of which constitute acroleine.

Acids.—When we examine the formulas of the fat acids, we are struck with a remarkable relation between them. Butyric, $C^8 H^8 O^4$; caproic, $C^{12} H^{12} O^4$; margaric, $C^{34} H^{34} O^4$, and all others, present different quantities of carbon and hydrogen for the same quantity of oxygen, but an equal proportion of carbon and hydrogen in each acid.

If we compare the alcohols, the æthers, &c. of these bodies, we

find the analogy holding good between them, as is more clearly shown in the following table, where each series is named by its acid, the acids having been most thoroughly investigated. The compounds are given in the hydrated state, and their empirical general formula at the top of the columns:—

	Æthers. $C^n H^{n+1} O$	Alcohols. $C^n H^{n+2} O^2$	Aldehydes. $C^n H^n O^2$	Acids. $C^n H^n O^4$	Boiling-point.
Formic ..	$C^8 H^3 O$	$C^2 H^4 O^2$	$C^2 H^2 O^2$	$C^2 H^2 O^4$	212°
Acetic....	$C^4 H^5 O$	$C^4 H^6 O^2$	$C^4 H^4 O^2$	$C^4 H^4 O^4$	248°
Acetonic..	.....	.....	.....	$C^6 H^6 O^4$	
Butyric ..	.....	.....	$C^8 H^8 O^2$	$C^8 H^8 O^4$	327°
Valeric ..	$C^{10} H^{11} O$	$C^{10} H^{12} O^2$	$C^{10} H^{10} O^2$	$C^{10} H^{10} O^4$	387°
Caproic ..	.....	.....	.....	$C^{12} H^{12} O^4$	396°
Œnanthylic	.....	.....	$C^{14} H^{14} O^2$	$C^{14} H^{14} O^4$	
Caprylic ..	.....	.....	.....	$C^{16} H^{16} O^4$	
Pelargonic	.....	.....	.....	$C^{18} H^{18} O^4$	
					Fusible at
Capric....	.....	.....	.....	$C^{20} H^{20} O^4$	64°
Cocinic ..	.....	.....	.....	$C^{22} H^{22} O^4$	95°
Lauric....	.....	.....	.....	$C^{24} H^{24} O^4$	113°
Myristic ..	.....	.....	.....	$C^{28} H^{28} O^4$	120°
Benic	.....	.....	.....	$C^{30} H^{30} O^4$	126°
Cetylic / Palmitic	$C^{32} H^{33} O$	$C^{32} H^{34} O^2$	$C^{32} H^{32} O^2$	$C^{32} H^{32} O^4$	133°
Margaric..	.....	.....	.....	$C^{34} H^{34} O^4$	140°
Benstearic	.....	.....	.....	$C^{42} H^{42} O^4$	160°

The butyric, valeric and œnanthylic aldehydes are severally known as butyral, valeral and œnanthal, but they seem to be only isomeric with those aldehydes; the formic is known only in acroleine and formomethylal. Cetylic æther is only known in combination.

When we compare the formulas of the above acids, the uniform equality in the equivalents of carbon and hydrogen is too evident to escape observation; and Dumas has endeavoured to show that the radical of each acid is an exact multiple of $C^2 H^2$. But, as Berzelius observes, he is obliged to add the equivalent of basic water to support his view; for the formula of the acid in combination with a base (dry acid) always shows 1 equiv. less of hydrogen than of carbon. Thus the formula of the dry butyric acid is $C^8 H^7 O^3$, that of the hydrated acid $C^8 H^8 O^4$. Hence Dumas could not apply his theory to the combined or dry acid. If we decompose these acids by distillation alone or with lime, we obtain an acetone, and by further action a carbohydrogen of the composition $C^2 H^2$, or an exact multiple of it.

A much simpler view of this series of acids, is to regard them as conjugates of formic acid. The formula of dry formic acid is $C^2 HO^3$, of dry acetic acid $C^4 H^3 O^3$, and by subtracting the former from the latter we have the carbohydrogen, thus $C^4 H^3 O^3 - C^2 HO^3$

$= C^2 H^2$. Formic, taken from valeric, $C^{10} H^4 O^3 - C^2 HO^3 = C^8 H^8 = 4C^2 H^2$; from margaric, $C^{34} H^{33} O^3 - C^2 HO^3 = C^{32} H^{32} = 16C^2 H^2$. The result is the same by abstracting hydrated formic acid from any of the other hydrated acids. From several of these acids, and from their alcohols, such carbohydrogens have been obtained, that of the acetic series being $C^4 H^4$, of the valeric $C^{10} H^{10}$, &c. When margaric acid is distilled, it appears that several margarones have been obtained of the composition $C^{33} H^{33} O$, $C^{34} H^{33} O$, $C^{46} H^{45} O$, $C^{68} H^{66} O$. Assuming it to be $C^{34} H^{33} O$, if we subtract it from $C^{46} H^{45} O$, there remains $C^{12} H^{12}$. And in like manner Bussy's margarone $C^{68} H^{66} O$, or $C^{68} H^{67} O$ appears to be common margarone with $C^{34} H^{34}$. Moreover, the oily body distilling at the same time with margarone is a polymeric $C^2 H^2$. That acetic acid may be regarded as formic acid with $C^2 H^2$ we may infer, although not assert positively, from its oxidation by periodic acid, whereby formic acid results. The olefiant gas derived from the acetic series is generally regarded as $C^4 H^4$; but Berzelius considers it a peculiar radical, which he terms elayle, with the formula $C^2 H^2$; and its various combinations and metamorphoses are as easily, perhaps better, explicable on the supposition that it is $C^2 H^2$.

Another reason why we may consider the series of acids as being the formic paired with multiples of $C^2 H^2$, lies in the uniformly successive change of properties from the lowest to the highest. Formic, acetic and acetonic are watery; butyric and valeric, oily; caproic, œnanthylic, &c., smeary fats, laurostearic, &c., solid and firm. The odour and taste of formic and acetic are most pungent; of butyric to caprylic, less odorous and pungent to the taste; the others, inodorous and tasteless. The first four acids are miscible with water; valeric is soluble in 30 parts water at 54°; caproic to caprylic, scarcely soluble; the rest insoluble. The boiling-points from formic to valeric rise in nearly equal proportions. The fusing-points from capric to margaric rise with nearly equal uniformity. The odour of formic and acetic are similar in character. Acetonic resembles the acetic closely in odour and in the properties of its compounds. Butyric has a mixed odour of butter and acetic acid.

It might be urged against this view, that stearic acid appears to be a lower oxide of the same radical as margaric. Thus 2 equivs. margaric (dry) $= C^{68} H^{66} O^6$, and stearic $= C^{68} H^{66} O^5$. The composition of crystallized stearic acid is $C^{68} H^{68} O^7$, or $C^{68} H^{66} O^5 + 2HO$, which water is replaced by 2 equivs. of base. A simpler view is to consider it as composed of margaric and margarous acids,

$$C^{68} H^{66} O^5, 2HO = C^{34} H^{33} O^3, HO + C^{34} H^{33} O^2, HO.$$

Hence its bibasic character. The distillation of stearic acid confirms this view, whereby margaric acid and margarone chiefly result; for 2 equivs. margarous acid, $C^{68} H^{66} O^4, 2HO$, are resolved into 1 equiv. of margaric acid and 1 equiv. of margarone, while water is given off,

$$C^{68} H^{66} O^4, 2HO = C^{34} H^{33} O^3, HO + C^{34} H^{33} O \text{ and } HO.$$

We ought therefore to obtain from 2 equivs. stearic acid, 3 equivs.

margaric acid and 1 equiv. margarone, which agrees well with Chevreul's results. We have other examples of a similar pairing of acids in the vaccinic, the dry acid $C^{20}H^{18}O^5 = C^{12}H^{11}O^3 + C^8H^7O^2$, which are caproic and butyrous acids, and are convertible into caproic and butyric acids by simple oxidation in the air. Again, the relation of tartaric or racemic to formic acid has been noticed by chemists both in formula and behaviour; and we may regard it as similarly constituted, except that one of the acids is anhydrous,

$$C^4H^2O^5, HO = C^2HO^3, HO + C^2HO^2,$$

which would be formic and dry formous acids. We may mention œnanthic acid as the œnanthylous acid is known in its anhydrous state, although by its reactions it may be viewed as œnanthylate of œnanthal.

It may also be urged against these views, that some acids do not show their conjugate to be an exact multiple of C^2H^2. Thus anamirtic acid is $C^{35}H^{35}O^4$, and palmitonic acid is $C^{31}H^{31}O^4$. But the former may consist of margaric and another acid not yet found; thus

$$C^{34}H^{34}O^4 + C^{36}H^{36}O^4 = 2(C^{35}H^{35}O^4);$$

and palmitonic may be half the sum of palmitic and benic acids.

The oxidation of the fat acids by nitric acid tends to confirm the views of their conjugate character. When stearic acid is heated with nitric acid, it is readily converted into margaric acid by a simple oxidation of its margarous acid. By the action of nitric acid on margaric or oleic acid, the whole series of volatile fat acids, from capric down to formic, have been obtained. To obtain these acids from oleic, Redtenbacher employed fuming nitric acid, warmed and distilled the liquid; the residue contained sebacic, succinic, &c. acids. To obtain these last, Bromeis recommends a strong acid diluted with half its weight of water, so that we may infer that the oxidation is less violent in the last case, and that hydrogen would be mainly acted on, while in the former both hydrogen and carbon will be oxidized. The following table of the less volatile acids remaining shows this fact. I have added sebacic acid derived from the dry distillation of oleine:—

	Empiric formula. $C^nH^{n-2}O^8$.	Acrylic.
Succinic ..	$C^8H^6O^8 = C^4H^2, C^4H^4O^8 = C^6H^4O^4 + C^2H^2O^4$	
Adipic....	$C^{12}H^{10}O^8 = C^4H^2, C^8H^8O^8 = C^6H^4O^4 + C^6H^6O^4$	
Pimelic ..	$C^{14}H^{12}O^8 = C^4H^2, C^{10}H^{10}O^8 = C^6H^4O^4 + C^8H^8O^4$	
Suberic ..	$C^{16}H^{14}O^8 = C^4H^2, C^{12}H^{12}O^8 = C^6H^4O^4 + C^{10}H^{10}O^4$	
Sebacic ..	$C^{20}H^{18}O^8 = C^4H^2, C^{16}H^{16}O^8 = C^6H^4O^4 + C^{14}H^{14}O^4$	

Succinic....	$C^8H^6O^8 = C^2O^4, C^6H^6O^4$,	formic.
Adipic	$C^{12}H^{10}O^8 = C^2O^4, C^{10}H^{10}O^4$,	acetonic.
Pimelic	$C^{14}H^{12}O^8 = C^2O^4, C^{12}H^{12}O^4$,	butyric.
Suberic	$C^{16}H^{14}O^8 = C^2O^4, C^{14}H^4O^4$,	valeric.
Sebacic	$C^{20}H^{18}O^8 = C^2O^4, C^{18}H^{18}O^4$,	œnanthylic.

The general formula indicates 2 equivs. less of hydrogen than of carbon, from which we may infer that by a feebler oxidation one-

half of the hydrogen from the conjugate $C^4 H^4$ of the fat acids is removed, leaving $C^4 H^2$, which remains united with one of the acids, in all probability formic acid, constituting acrylic acid. Abstracting the conjugate $C^4 H^2$, we observe by the third column that the first two and last two acids may consist severally of 2 equivs. formic, acetic, acetonic and butyric acids. But the pimelic would leave $2C^5 H^5 O^4$, which obliges us to consider it as composed of formic and butyric, or of acetic and acetonic. Since we have good reason for believing acrylic acid, $C^6 H^4 O^4$, to be formic acid with $C^4 H^2$, we prefer considering all the above as composed of acrylic and another of the fat acids, according to which view the fourth column is constructed. This view of the double acid constitution of the above acids sufficiently accounts for their bibasic character, 2 equivs. water being replaced by 2 equivs. base.

By examining the composition of oleic and moringic acids, we find the same relation of carbon and hydrogen, $C^n H^{n-2}$; for oleic $= C^{36} H^{34} O^4$, and moringic $= C^{30} H^{28} O^4$. But they form monobasic acids. By subtracting acrylic acid from them, we have $C^{30} H^{30}$ for the former, and $C^{24} H^{24}$ for the latter as their conjuncts. Now the behaviour of oleic acid refers it to the other fat acids, from which its formula must exclude it unless we adopt the above view. Moreover, the formation of sebacic acid by the distillation of oleine is readily accounted for. We may then consider the oleic acids as acrylic acid with the usual copula $C^2 H^2$, or an exact multiple of it. It may hereafter be shown that other of the fat acids, besides the formic, unite with $C^4 H^2$, so that we may have a series of acrylic acids.

Before leaving this subject, the views of Millon on the above acids, probably derived from those of Mitscherlich on benzoic acid, should be noticed. I have therefore placed his formulas in the lower table, to which list he adds oleic and moringic acids. But it may be objected against his view, that the basic water is wholly left out of view, and is sufficient to refute his theory. How does his view explain the fact that 2 equivs. CO^2 neutralize 1 equiv. base in an oleate?

The view above taken of the constitution of this series of acids certainly presents the advantage of greater simplicity, which is desirable, if consistent with facts. According to the views commonly received, we must adopt two radicals in the formic series, methyle $C^2 H^3$ and formyle $C^2 H$; two at least in the alcohol series, ethyle $C^4 H^5$ and acetyle $C^4 H^3$; two in the valeric series, amyle $C^{10} H^{11}$ and valeryle $C^{10} H^9$; and thus we should have in the seventeen series of the above table no less than thirty-four radicals, and if we should add mesityle in acetone, fifty-one radicals.

By adopting the above views, we may employ but two radicals for the whole series, methyle, $C^2 H^3$, and formyle, $C^2 H$. For acetyle would be formyle with the carbohydrogen, $C^2 H + C^2 H^2 = C^4 H^3$; amyle would be formyle with 4 equivs. of the carbohydrogen, $C^2 H + C^8 H^8 = C^{10} H^9$; and so of the rest of the acids and aldehydes. Instead of ethyle we would have methyle with the carbo-

hydrogen, $C^2 H^3 + C^2 H^2 = C^4 H^5$, instead of amyle the same with 4 equivs. of carbohydrogen, $C^2 H^3 + C^8 H^8 = C^{10} H^{11}$. In short, the æther and alcohol of each series would be methylic æther and alcohol, paired with exact multiples of $C^2 H^2$. The aldehyde and acid of each series would be formic aldehyde and acid, paired with the same carbohydrogen. All the facts known in reference to the combinations and transformations of the various bodies in the above tables, as far as I have been able to obtain them, are as readily explicable on this view as by the theories commonly adopted.—*Journal of the Franklin Institute*, May 1848.

On the Nitrites. *By* N. W. Fischer.

Nitrite of Potash.—In the preparation of this salt, by heating saltpetre to redness it always retains some nitrate of potash, while it is at the same time contaminated by a certain amount of free alkali. It may be purified from both in the following manner:—The sufficiently-ignited saline mass is dissolved in boiling water, and the solution set aside for twenty-four hours, upon which it is decanted from the nitre which has crystallized. The free potash contained in it is saturated with vinegar, and twice its volume of alcohol then added to it. In the course of a few hours some more nitre crystallizes from the solution, and the liquid separates into two strata; the upper one is a solution of acetate of potash in alcohol; the lower one is an aqueous solution of nitrite of potash, from which the salt separates in crystals of an indistinct form when dried *in vacuo* over sulphuric acid; the crystals soon deliquesce.

Nitrite of Soda is formed more easily than the potash salt on heating the nitrate of soda; but it contains a much larger amount of free alkali, from the nitrate of soda being more readily decomposed than the nitrate of potash. It is treated in the same manner as the potash salt; but in this case the spirituous liquid does not separate into two layers, but the solution contains some acetate and nitrate of soda along with the nitrite; it is therefore evaporated to dryness, and the mass exposed to the air, when the nitrite of soda deliquesces, and may be poured off. When placed over sulphuric acid, the salt separates from the ley in crystals. It differs from the potash salt principally in being soluble in alcohol.

Nitrite of Baryta.—The ignited nitrate of baryta is dissolved in water, carbonic acid passed into the solution to separate the free baryta, the filtered liquid evaporated to dryness, and the residue dissolved in as little water as possible. Upon this twice the amount of alcohol is added to it, when the greater portion of the nitrate of baryta is separated; the remainder crystallizes, on slow evaporation, from the spirituous solution. The salt is obtained in two forms, in six-sided regular prisms and in isoclinic prisms. The salt is not altered by exposure to the air, and dissolves readily in water and in alcohol.

Nitrite of Strontia is obtained in the same manner as the baryta salt, but the alcoholic solution must be evaporated much further to

separate the nitrate. The salt separates in slender needles, which quickly absorb moisture and deliquesce.

Nitrite of Lime.—This salt could not be obtained pure by the process detailed for the two previous salts; it was prepared by means of the nitrite of silver; the silver salt, dissolved in boiling water, was precipitated with lime water; the liquid filtered from the oxide of silver still contains some silver salt along with the lime salt, owing to the formation of a double nitrite of silver and lime; the liquid is therefore treated with sulphuretted hydrogen, and then with carbonic acid, in order to separate the silver and the excess of lime, and the filtered solution is evaporated at a gentle heat. The lime salt crystallizes in prisms and deliquesces in the air; it is insoluble in absolute alcohol.

Nitrite of Ammonia was prepared by decomposing nitrite of silver with chloride of ammonium. It is advantageous to employ less chloride of ammonium than is required to precipitate the whole of the silver. A residue of silver may still remain in the salt obtained by crystallization, if not previously separated by sulphuretted hydrogen, owing to the production of a double salt.

Nitrite of Magnesia is easily obtained by boiling the silver salt with calcined magnesia; but the solution filtered from the precipitated oxide of silver and excess of magnesia must likewise be treated with sulphuretted hydrogen, to separate a trace of silver. Its solution must not be evaporated by heat; by desiccation over sulphuric acid, it is obtained as a laminar, deliquescent, saline mass, which is readily decomposed by heat and is insoluble in absolute alcohol.

Nitrite of Silver, obtained by double decomposition with one of the previously described alkaline or earthy nitrites, forms a powder consisting of slender crystals, which are white, but in a mass appear yellow; they are prisms of 59°, with oblique terminal surface, probably triclinic; they may be obtained several inches in length by allowing the hot saturated solution to evaporate spontaneously in the dark. It dissolves with considerable ease in boiling water, but very sparingly in cold; and may therefore be prepared with the impure nitrites of the alkalies and easily purified.

The other nitrites of the metallic oxides are in general crystalline and very easily decomposed. The salts of zinc, cadmium, lead, copper and cobalt are obtained by acting with these metals upon the solution of nitrite of silver; tin, mercury and antimony reduce the silver without producing the corresponding salt; iron and nickel do not reduce the silver from the solution of the nitrite. Nitrite of copper and lead are decomposed on evaporating their solutions; the first forms an insoluble basic salt, which separates in blue scales.

The author also obtained the following double salts:—

Nitrite of Silver and Potash was prepared by mixing nitrate of silver with an excess of nitrite of potash; at first either no precipitate of nitrite of silver is formed, or if formed, it again dissolves; and when the solution is concentrated, the double salt separates immediately. If the salt is prepared by evaporating dilute solutions, the temperature should not exceed 86°–104°. It crystallizes partly

in horizontal prisms and partly in rhombic octahedrons; it is of a yellowish colour, is not altered by exposure to the air, and experiences a slight decomposition even at a gentle heat, being decomposed into the silver and potash salt; when heated more strongly, the silver salt is decomposed, nitrous acid is disengaged, and metallic silver remains with the undecomposed potash salt. Water acts in the same manner; the salt is decomposed into the two salts of which it consists, the water dissolving the potash salt and depositing the silver salt excepting mere traces. It is owing to this that the salt when treated with water loses its transparency and crystalline form; and for the same reason it cannot be obtained when a very dilute solution of nitrate of silver or of the nitrite of potash is employed. The other nitrites of the alkalies and alkaline earths form similar double salts with the nitrite of silver.

Nitrite of the Protoxide of Palladium and Potash is obtained by mixing the protochloride or protonitrate of palladium with an excess of nitrite of potash. It falls as a white powder from concentrated solutions, and is obtained in yellow crystals on evaporating dilute solutions. It crystallizes in three forms,—1st, in prisms of $61\frac{1}{2}°$ with several oblique surfaces; 2nd, in rhombic prisms, belonging to the triclinic system, with several marginal surfaces; 3rd, the beautiful *red* crystals obtained in one experiment along with the yellow ones were six-sided prisms. The crystals 2 and 3 are permanent in the air, while the 1st effloresce and become opake. The double salt dissolves with tolerable ease in water, and is decomposed by heat like the silver salt, *i. e.* the palladium is reduced, nitrous acid is given off, and the nitrite of potash is left unaltered.

Nitrite of Lead and Potash is obtained in the same manner as the preceding; it is yellow, easily soluble, and crystallizes in six-sided prisms, belonging to the monoclinic system.

Nitrite of Nickel and Potash is obtained in the same manner as the preceding salts, but its preparation is less certain; even the most gentle heat must be avoided. It forms beautiful small octahedrons of a brownish-red colour, which dissolve readily in water with a green colour.

Nitrite of Cobalt and Potash is instantly precipitated on mixing a solution of cobalt with one of nitrite of potash. It forms a yellow amorphous powder, is perfectly insoluble in water, experiences the same decomposition by heat as the preceding salts, with this difference, that the residue contains *peroxide* of cobalt along with the nitrite of potash. The nitrite of potash is therefore not only a sure and sensitive test for cobalt, producing in a solution containing $\frac{1}{1000}$th cobalt instantly, and in one containing $\frac{1}{3000}$th after a few hours this yellow precipitate, but it is also adapted for the separation of cobalt from nickel, and possibly from other metals with which it may be contained in a solution, as these metals either enter into no combination with nitrous acid or form easily soluble compounds; moreover, this cobalt salt is scarcely attacked by acids or ammonia at a mean temperature; so that when the solution filtered from the precipitate is evaporated to dryness, in order to separate the last traces

of cobalt, the other metallic oxides, oxide of nickel, &c., contained in the residue may very easily be separated.—Poggendorff's *Annalen*, lxxiv. p. 115.

On the Separation of the Alkalies from Magnesia by the Carbonate of Silver. *By* F. Sonnenschein.

Pure oxide of silver is extremely well adapted for the purposes of quantitative analysis, not only because it is a very powerful base, but because it may also be again easily separated. Its preparation however by precipitation with potash or soda is insofar accompanied with difficulty, as it requires very considerable time to remove the excess of the precipitant by washing; on which account I employ the carbonate for separating the alkalies from magnesia.

For this purpose the compounds to be separated are converted in the usual manner into chlorides, which are evaporated to dryness, and then faintly heated to redness, when any ammoniacal salt contained in the solution, as well as a portion of the muriatic acid combined with the magnesia, escape. When the dry mass is cooled, water is poured over it, and it is then boiled with carbonate of silver until the liquid has a strong alkaline reaction. The boiling is continued for about ten minutes, stirring the whole time, when the decomposition is complete. The solution is then filtered as hot as possible, and the precipitate washed with hot water. The filtered liquid now contains only the alkalies and a trace of the silver salt, which is removed with muriatic acid; and the alkalies are then determined in the usual manner. The residue left upon the filter is digested with muriatic acid, and after removing the chloride of silver, the magnesia precipitated with phosphate of soda and ammonia.

The carbonate of silver is preferable to all the other compounds of silver, for instance the acetate or nitrate, because the chloride of magnesium is immediately converted by it into an insoluble compound, which on employing the other salts has to be attained in a round-about way. The salt is best prepared for this purpose by carefully precipitating the nitrate of silver with carbonate of ammonia; after subsidence the precipitate is easily freed from the ammoniacal salt by the frequent addition of water and decantation; it is not necessary to filter it or to dry it, as the moist precipitate is more easily decomposed.—Poggendorff's *Annalen*, lxxiv. p. 313.

On some Compounds of the Oxide of Amyle. *By* M. Rieckher.

The compounds of the oxide of amyle have been mostly examined by Dumas, Stass, Cahours and Balard. M. Rieckher has recently published a memoir on this subject, from which we abstract the following:—

Oxide of Amyle (amylic æther).—Balard attempted in vain to prepare this body from potato fusel oil by treatment with various

acids. When fusel oil and sulphuric acid are mixed together, a small quantity of a substance immediately separates; on raising the temperature slightly above 212°, sulphurous acid is given off, and there finally remains a pitchy black residue. The distillate, after removing the sulphurous acid by agitation with bichromate of potash and drying it over chloride of calcium, exhibited the composition of a mixture of oxide of amyle and fusel oil. On mixing it with concentrated sulphuric acid, part of it dissolved, while another portion floated on the surface. The latter was removed, and the portion dissolved in sulphuric acid precipitated by the addition of water, deprived of acid and dried. The liquid was submitted to a fractional distillation, and that which passed over between 347° and 361° analysed. It furnished—

Carbon	76·10	76·08	10	76·17
Hydrogen	13·82	..	11	13·78
Oxygen	..	..	1	10·05

The specific gravity of this compound is 0·779 at 72°; the density of its vapour was not determined. The high boiling-point of this body shows however that it cannot stand in the same relation to amylic alcohol as æther does to alcohol. As is well known, Balard obtained, by heating protochloride of amyle with an alcoholic solution of potash, a liquid which boiled between 232° and 234°, which he describes as amylic æther.

Nitrite of the Oxide of Amyle was obtained by the author by passing nitrous acid into fusel oil, and heating it on the water-bath. This compound boils at 196°; its specific gravity is 0·877, and its formula $C^{10} H^{11} O, NO^3$. It is but slowly decomposed by dry caustic potash, more quickly by an alcoholic solution, and in a short time nitrite of potash can be detected. When added in drops to hydrate of potash in a state of fusion, it yields valerianate of potash; when heated with peroxide of lead, it furnishes nitrate and nitrite of lead and fusel oil.

Nitrate of the Oxide of Amyle is obtained by carefully distilling 1 vol. (?) fusel oil, 2 vols. pure nitric acid, and from 20 to 30 grs. of urea or of nitrate of ammonia. The liquid, deprived of acid and water, boiled at 278°; its specific gravity was found to be 0·902, and its composition—

Carbon	45·00	45·26	10	45·34
Hydrogen	8·45	8·52	11	8·20
Nitrogen	..	..	1	10·58
Oxygen	..	..	6	35·88

Benzoate of the Oxide of Amyle.—1 part fusel oil and 2 parts sulphuric acid distilled with benzoate of potash furnish a liquid which boils between 485° and 489°, of a peculiar odour and the following composition:—

Carbon	75·39	75·62	75·27	24	75·21
Hydrogen	8·40	8·53	8·59	16	8·20
Oxygen	..	..	..	4	26·59

The author reobtained from this compound, as also from the oxalate and acetate of the oxide of amyle, fusel oil by decomposition with solution of caustic potash, which he submitted to analysis.

Cyanurate of the Oxide of Amyle, obtained by passing cyanic acid into fusel oil and purified by recrystallization, afforded on analysis 18·78–18·37 per cent. nitrogen, leading to the formula $2(Cy^3 O^3) + 3(C^{10} H^{11} O) + 3HO$, which requires 18·18 per cent. nitrogen.

Schlieper found, by the complete analysis of the cyanurate of the oxide of amyle dried at 212°, the formula $2(Cy^3 O^3)$, 3Ay1O + 9 aq, according to which it contains 16·1 per cent. of nitrogen. Whether these are two distinct compounds, or whether the difference depends upon the degree of temperature employed in drying, cannot be determined from existing data.

Lastly, the author prepared the protochloride of amyle by passing muriatic acid into fusel oil, and found in the product, which boiled at 216°, 22·85 and 23·26 per cent. of chlorine.—*Jahrb. für Prakt. Pharm.*, xiv. p. 1.

Observations on Corydaline. By M. Ruickholdt.

This substance had been previously examined by Wackenroder, Peschier and Winckler. The author has recently published the following observations on its composition and preparation:—*Radix aristolochiæ cavæ* is coarsely pounded, then repeatedly digested with 8 times the amount of water, containing 1 per cent. of muriatic acid, for three days in the cold. The united extracts are left for some time in contact with a few ounces of hydrate of lime, and the filtered solution mixed with carbonate of soda, which produces a slight greenish-white precipitate. As the filtered solution still afforded an abundant precipitate with tincture of galls, it was concentrated with muriatic acid, when a green resinous mass separated, and the decanted liquid deposited in a few days a crystalline substance. The resinous mass dissolved, with the exception of a black substance, in muriatic acid. The author considers it to be altered corydaline. The crystalline substance above mentioned dissolves for the greater part in hot alcohol, from which it separates on cooling in a mass resembling sulphate of quinine.

The lime precipitate first obtained, and likewise that produced by carbonate of soda, yielded a considerable quantity of corydaline to hot alcohol, and on evaporation a greenish-brown brittle mass remained. It was purified by solution in muriatic acid, precipitation with carbonate of soda, and again dissolving it in spirit. On evaporating this solution, a dirty green, somewhat brittle opake mass remained, the composition of which was found to be—

Carbon	60·19	45 =	59·59
Hydrogen	5·90	27	5·89
Nitrogen	3·02	1	3·09
Oxygen	30·89	18	31·43

Wackenroder adds to the above statements, that the crystals of corydaline form right rhombic prisms, with a six-sided terminal surface of a vitreous lustre. They are yellowish-green, brittle, and possess a bitter taste. They dissolve readily in alcohol, and again separate, in the course of a few days, in a crystalline state.

The solution of corydaline is precipitated by ammonia; caustic soda yields a precipitate, which however dissolves readily in an excess. The crystals of the muriate of corydaline lose 12·5 per cent. of water at 212°, and 3 per cent. more between 293° and 338°. They contain 10·78 per cent. of muriatic acid, with which the formula advanced by Ruickholdt does not agree.—Liebig's *Annalen*, Dec. 1847.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Formation of Hydraulic Limestones, Cements, and other Minerals in the Moist Way. By Prof. KUHLMANN.

THE author had some time ago observed that all limestones contain small quantities of alkalies; and he has recently found that in hydraulic limestones in particular a very considerable amount of potash occurs. From this he concluded that the silicate of potash must exercise an essential influence upon the production of cements; and he succeeded in producing artificially hydraulic limestone in the moist way, by mixing lime with silica or alumina dissolved in water containing some potash. When powdered chalk is employed for this purpose, the pasty mass obtained gradually hardens in the air, and attains equal hardness with the very best hydraulic cements. If, on the other hand, chalk in pieces or porous limestone is dipped into a solution of silicate of potash, they acquire, after several days' exposure to the air, such a degree of hardness at the surface that they scratch limestone; they admit of being polished, but it is only with porous stones that the hardening penetrates through the entire mass. This property may be usefully employed in the manufacture of ornaments, as by judicious treatment the surface experiences no alteration. The silification may even be employed for obtaining lithographic stones from chalk.

Gypsum is likewise hardened in the same manner, and its decomposition by alkaline silicates takes place far more rapidly and more completely. Crystallized gypsum is only superficially acted upon by it; but when ground and mixed with silicate of potash, it acquires a hard and shining surface. If too concentrated solutions are employed, the decomposition is too rapid, and the surface exfoliates after several days' exposure to the air. Oxide of manganese and potash may be employed with the same effect as the silicate of potash. The author ascertained by experiments that lime has the pro-

perty of precipitating metallic oxides dissolved in alkalies; as, for instance, oxide of copper from its solution in ammonia. He observes, on this subject, that in general every insoluble salt in contact with a saline solution, the acid of which forms with the base of the insoluble salt a still more insoluble combination, produces a decomposition of the salt in solution, which however in most cases is incomplete. Thus white lead precipitates a considerable quantity of chromate of lead from a cold solution of chromate of potash; silicate of potash and chromate of lime yield some silicate of lime, &c.

The carbonic acid of the atmosphere acts a principal part in the hardening of these artificial stones, and on its exclusion they do not become hard. The silicate of potash contained in the mass is decomposed by the carbonic acid; silicic acid separates, which contracts, and so assists considerably the solidification.

When a solution of silicate of potash is exposed to the air, it solidifies in the course of fourteen days to a transparent jelly, which gradually becomes very hard without losing its transparency; and after the lapse of several months it is capable of scratching glass.

The author is inclined to suppose that the crystallized silicic acid in the limestone rocks, as also flints, agates, &c., owe their origin to this cause; that they have consequently been formed by the decomposition of the silicate of potash by carbonic acid. In fact, he found, in examining these minerals, that, after ignition and pulverization, they communicated a decidedly alkaline reaction to water. In these siliceous deposits the two following causes have been principally active:—

1. Decomposition of the earthy carbonates by alkaline silicates, producing earthy silicates, which are decomposed under certain circumstances by water containing carbonic acid, and part with the earths.

2. Direct deposition of silicic acid by decomposition by carbonic acid of the alkaline silicate held in solution in water.

The author finds a confirmation of his view in the circumstance, that, besides the minerals previously mentioned, manganese, dolomite, talc, asbestos, emerald, corundum, sulphuret of antimony, &c., contain small quantities of alkalies.—*Ann. de Chim. et de Phys.*, xxi. p. 364.

How to harden Gypsum.

It is known that calcined gypsum, after being moistened with a solution of alum and again burnt, acquires much greater hardness and solidity. M. Kreating recommends for the same purpose a solution of 1 lb. of borax in 9 lbs. of water, which is poured over the calcined fragments of gypsum. They are then kept at a strong red heat for six hours, ground to a powder and worked. The effect is said to be still better if a pound of tartar and twice the quantity of water are added to the solution.—Liebig's *Annalen*, Dec. 1847.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Phosphates. *By* T. Fleitmann *and* W. Henneberg.

The ammonio-phosphate of soda gradually loses at a high temperature ammonia and water, forming at a certain period a dry, white saline mass, which dissolves wholly in water, and has a strong acid reaction. Subsequently, after the escape of more water, the acid reaction disappears; the mass now no longer dissolves entirely in water, but a portion remains undissolved; at a red heat this product fuses to a colourless liquid, which when rapidly cooled solidifies to a perfectly colourless and transparent glass of metaphosphate of soda, which scarcely possesses an acid reaction.

Graham has distinguished three modifications of the metaphosphate of soda; the vitreous one just mentioned, produced by a red heat, which does not redden litmus, dissolves very readily in water, and deliquesces even by exposure to the air; and two others, which are produced at a lower temperature, of which the one formed at a moderate heat is soluble, the other at a higher temperature is insoluble in water.

The modification of the metaphosphoric acid contained in the last insoluble salt is characterized by all its salts being insoluble in water. Maddrel*, who has submitted them to a more accurate examination, prepared them generally by mixing solutions of metallic oxides with phosphoric acid, evaporating and heating to 601°. They possess according to him the formula $MO + PO^5$.

The authors have now selected the soluble soda salt, which, as above mentioned, is produced on heating the ammonio-phosphate of soda as the starting-point for further investigation; and with the aid of this salt they have prepared a series of others, which form the subject of the present communication.

When the ammonio-phosphate of soda is heated until the whole of the water is expelled and the acid reaction of the mass has disappeared, the residue consists, if the heat has not been raised sufficiently to fuse the mass, of two salts, one of which is soluble and the other insoluble. The relative amount of the two salts varies; the production of the insoluble soda salt is avoided as carefully as possible by applying a slow and uniform heat. The best method of

* Chem. Gaz., vol. v. p. 26.

obtaining the largest amount of the soluble compound is to remove the heated mass, while it still has a strongly acid reaction, from the fire, to reduce it to powder, and then to heat it again, constantly stirring it, and taking care that the mass does not cake together. When the saline mass has but a faint acid reaction, it is allowed to cool, and then exhausted with cold water. If the solutions of the salt thus obtained are evaporated in shallow vessels at a temperature of 86°, the salt is obtained in beautiful crystals of the triclinometric system. The salt also crystallizes from a hot saturated solution on cooling.

The Soda Salt, $NaO, PO^5 + 4HO$ (air-dried), dissolves in 4·5 parts of cold water, and has a cooling pure saline taste, while the vitreous metaphosphate of soda has an insipid taste; it keeps for a long time unaltered in a cold aqueous solution. On boiling, it exhibits after some time an acid reaction, and the metamorphosis of the salt now proceeds rapidly. Nitrate of silver then yields a white precipitate, which becomes yellow on the addition of a drop of ammonia. The salt is insoluble in alcohol, and very sparingly soluble even in very weak spirit; which behaviour may be turned to account in obtaining beautiful crystals from very dilute solutions of the salt.

In the analysis the salt was converted by boiling with muriatic acid into ordinary phosphate of soda, and the phosphoric acid separated with a salt of magnesia. The excess of magnesia was removed from the alkali by solution of baryta, or by employing the method with oxide of mercury. Berthier's process of estimating the phosphoric acid gave in the present case very inaccurate results. The following are the numbers obtained by analysis:—

NaO	22·43	..	..	1	=31	22·30
PO^5	51·80	..	..	1	72	51·80
HO	25·92	25·81	26·08	4	36	25·90

This salt does not melt in its water of crystallization, the greater part of which it loses over sulphuric acid and in the water-bath.

The Silver Salt, $3(AgO, PO^5) + 2HO$ (crystallized), is obtained by adding nitrate of silver to a tolerably concentrated solution of the soda salt. The salt soon begins to separate, and appears, especially when an excess of metaphosphate of soda is employed, in beautiful transparent crystals belonging to the monoclinometric system. It easily retains some soda salt, owing to its great tendency to form double salts. It does not decrease in weight over sulphuric acid. In the water-bath it loses about half its amount of water, when it acquires an acid reaction, and absorbs from the air more than 3 per cent. of water, which it does not lose again at 212°. It appears consequently to pass into the ordinary metaphosphate of silver, which in one experiment, when dried at 212°, afforded 4·41 per cent. of water, which corresponds pretty accurately to 1 equiv. The analysis of the hydrated salt gave—

AgO	58·62	..	..	3	=348	59·80
PO^5	38·21	..	..	3	216	37·11
HO	3·17	3·02	3·11	2	18	3·09

The Lead Salt, PbO, PO^5 + HO (air-dried), is obtained in a similar manner to the silver salt. It dissolves less easily in water, and is always obtained in smaller crystals. The salt very frequently contained a trace of nitrate of lead, with which it had been prepared. The air-dried crystals furnished on analysis—

PbO	58·10	..	..	1 =	111·6	57·92
PO^5	36·83	..	..	1	72·0	37·40
HO.....	5·07	4·86	5·07	1	9·0	4·68

The Baryta Salt, BaO, PO^5 + 2HO (air-dried), is obtained by dissolving 1 part of the soda salt in from 10 to 15 parts of water, and adding to it an almost saturated solution of 2 to 3 parts of chloride of barium. After standing for some time, the mixture affords beautiful oblique rhombic prisms. In the water-bath it loses only one-third of its water, and gradually acquires an acid reaction. It requires a higher temperature to expel the remainder, so that the formula of this salt may perhaps be expressed in the following manner:—3(BaO, PO^5) + 4HO + 2HO. The salt does not melt at a red heat, but is rendered insoluble in acids. In the analysis of the air-dried salt, the total amount of water found was 10·83 and 11·07 per cent., of which, in a third experiment, 4·12 per cent. were expelled in the water-bath and 6·76 by subsequent ignition. The ignited or anhydrous salt afforded 52·15 and 52·19 per cent. of baryta, and 48·43 per cent. phosphoric acid, leading to the formula BaO, PO^5 for the anhydrous salt, and to that above given for the hydrated one.

A double *Salt of Baryta and Soda*, 2BaO, NaO, $3PO^5$ + 8HO (air-dried), is obtained by the same process as the preceding salt, except that the relative quantities of the materials employed are the reverse. It crystallizes in stellate groups, and is more easily soluble in water than the preceding salt. In the water-bath it lost 9·86 per cent., or 5 equivs. of water; the remaining 5·58 per cent., or 3 equivs., were expelled at a higher temperature, when the salt did not puff up like the preceding. The total amount of water found in the analysis was 15·49 and 15·29 per cent.; and the anhydrous salt consisted of—

BaO	38·74	38·76	2 =	153·2	38·28
NaO	7·58	..	1	31·0	7·75
PO^5	54·03	..	3	216·0	53·97

In other experiments, employing the baryta and soda salt in such proportions that a double salt might have been formed of equivalents of the two bases, the last salt was always obtained. In preparing the double salts of zinc and lime, the salts produced always contained for 1 equiv. NaO 2 equivs. of the other base.

It is especially worthy of attention that none of the salts described above could be obtained anhydrous in the water-bath. But this amount of water is not at all necessary to the constitution of the salt; for even the fused metaphosphate of soda may be reconverted by very slow cooling into the crystalline soda salt. This behaviour indeed offers a very excellent means of obtaining the crystalline soda

salt, with which the salts above described were prepared. For instance, the salt is very easily obtained by surrounding large quantities of the fused metaphosphate of soda in a platinum crucible with one or several Hessian crucibles, heating the mass to fusion in a charcoal fire, and then allowing it to cool slowly in the furnace. In this manner a very beautiful crystalline mass is obtained. On dissolving it in hot water, avoiding a large excess, the liquid separates into two layers, the larger one of which contains the crystalline salt; the other layer is undoubtedly a solution of unaltered metaphosphate of soda. When agitated it becomes milky, but soon separates into the two layers again; a clear mixture is obtained only after the addition of a large quantity of water.

The most natural explanation of this behaviour appears to be, that on slow cooling, the temperature which is requisite for the production of the crystalline salt can extend over a considerable length of time; but then, owing to the partially hastened cooling, the cold mass should afford along with the unaltered vitreous metaphosphate of soda a corresponding amount of the insoluble soda salt, the production of which, as above stated, takes place, as regards the temperature, between that of the crystalline and amorphous salt. Not a trace of this insoluble salt however was observed.

On the Constitution of the Phosphates.—We are now more accurately acquainted with three distinct modifications of metaphosphoric acid. That contained in the series of salts examined by Maddrel forms insoluble salts which contain no water. The modification which gives rise to Graham's easily soluble viscid salts has not yet been examined as regards the amount of water contained in its salts. With respect to the third modification which has been investigated by the authors, it appears that a conclusion may be drawn from the amount of water contained in these salts as to the constitution of this modification.

If we consider the amount of water in the above-described salts, especially in those dried in the water-bath, in its relation to 1 equiv. base, we find for instance—

$$AgO\,PO^5 + \tfrac{2}{3}HO;\quad BaO\,PO^5 + \tfrac{4}{3}HO;\quad NaO\,PO^5 + \tfrac{1}{6}HO.$$

These expressions, in conjunction with the formulæ of the double salts, necessarily lead us to express the rational formulæ of the salts belonging to the series of the crystalline metaphosphate of soda in the following manner:—

Soda salt	$3NaO$	$3PO^5 + \frac{1}{2}HO + 11\frac{1}{2}HO$
Silver salt	$3AgO$	$3PO^5 + 2HO$
Lead salt	$3PbO$	$3PO^5 + 3HO$
Baryta salt	$3BaO$	$3PO^5 + 4HO + 2HO$
Baryta and soda salt ..	$2BaO\,NaO$	$3PO^5 + 3HO + 5HO$

and to admit in these salts a complex phosphoric acid, constituted of 3 atoms of phosphorus and 15 atoms of oxygen. It is certain that for the other two modifications of the metaphosphoric acid the numbers will be found by which the formula PO^5 should be multiplied, to give the corresponding complex acids. As is well known, the

present usual mode of viewing the phosphates as combinations of the formulæ $3MO + PO^5$; $2MO + PO^5$; $1MO + PO^5$, in which MO may also represent water, was proposed by Graham. Liebig, in his treatise on the constitution of organic acids, was the first to draw attention to the fact that such an assumption was incompatible with theory. If we admit that, in order to become acquainted with the nature of acids, we must ascertain how much acid combines with the same quantity of base, we obtain from the series of the phosphates the following formulæ, instead of Graham's: $6MO + 2PO^5$ (ordinary phosphates); $6MO + 3PO^5$ (pyrophosphates); $6MO + 6PO^5$ (metaphosphates), assuming that the different properties of the acids are produced by the elements of the formula PO^5 being multiplied with 2, 3 .... 6 in the modifications hitherto known of phosphoric acid; and on this view ordinary phosphoric acid passes into pyrophosphoric or metaphosphoric acid, accordingly as the atom $2PO^5$ unites with $1PO^5$ or $4PO^5$ to a new atom. Now these last acids can be obtained from the first by the addition of anhydrous phosphoric acid in suitable proportions, and pyrophosphate of soda by fusing together $3NaO\,PO^5$ and $NaO\,PO^5$.

From the facts hitherto known no opinion can be formed as to the absolute atomic weight of phosphoric acid, as the usual formula of the ordinary phosphoric acid $PO^5 + 3MO$ can certainly not yet be proved to be unsatisfactory. The metaphosphoric acid, represented in the previous series of salts by the formula $6MO + 6PO^5$, may in fact be modified as follows:—

$$MO + PO^5;\ 2MO + 2PO^5;\ 3MO + 3PO^5, \&c.$$

The authors have assigned the last of these three formulæ to the salts described by them.

As the view that the phosphoric acids form complex atoms was rendered more probable by the above investigation, the authors sought to ascertain whether the gaps existing in the above-mentioned series for the *a*, *b* and *c* phosphoric acids might be filled by the discovery of the acids which should occupy those positions. In the above series, in which the phosphoric acids were referred to 6MO, there are evidently still missing the two members $6MO + 4PO^5$ and $6MO + 5PO^5$ to render it complete from the ordinary phosphoric acid $6MO + 2PO^5$ to the metaphosphoric acid $6MO + 6PO^5$. The authors have obtained the salts of both these acids.

For preparing the salts of the formula $6MO + 4PO^5$, the soda salt of this series, produced by fusing together 76·87 parts of metaphosphate of soda (Graham's fused salt) with 100 parts anhydrous pyrophosphate of soda, was employed. The two salts may be fused in a platinum crucible over an Argand lamp in the above proportions, or a mixture of 187·27 parts of the same metaphosphate of soda with 100 parts of the compound $3NaO\,PO^5$. The fused mixture solidifies on cooling to a white crystalline mass; it is reduced to powder, and quickly exhausted with water, for on long digestion the ordinary phosphates are obtained. If the hot solution filtered from the residue is placed over sulphuric acid to crystallize, fre-

quently from twelve to twenty-four hours elapse before crystallization commences. It is best to evaporate the mother-ley to dryness, to fuse the residue, and then treat it as above, as products of decomposition are easily obtained by mere evaporation; for the salt $6NaO, 4PO^5$ very readily splits into the compounds $2NaO, HO, PO^5$, which is more sparingly soluble and separates with the salt $6NaO, 4PO^5$, and $NaO\,2HO, PO^5$, which is deliquescent, and is consequently readily soluble. The latter has an acid reaction, and very much hastens the transformation of the remainder.

The Soda Salt, $6NaO + 4PO^5$, dissolves in about 2 parts cold water, and has a faint alkaline reaction. In solutions of the salt this reaction soon passes into an acid one, and the latter again into the alkaline on fusing the residue after evaporation to dryness. The salt afforded on analysis—

NaO.....	40·05	..	..	..	6=186		39·24
PO^5.....	60·05	60·45	60·98	60·47	4	288	60·76

If the mixture which produces the salt $6NaO + 4PO^5$ is dissolved in water instead of being fused, the pyrophosphate of soda separates unaltered on crystallization; the soda salt just described cannot be obtained in this manner. This behaviour shows that the salt $6NaO + 4PO^5$ is not a mere double salt of pyrophosphate and metaphosphate of soda; at the same time the silver and magnesia salts corresponding to the soda salt, demonstrate that it is a simple salt, for the metaphosphate of silver is very readily soluble in an excess of metaphosphate of soda, while the pyrophosphate of silver is insoluble both in pyrophosphate and in metaphosphate of soda; if consequently the silver precipitate of the salt $6NaO, 4PO^5$ consisted of pyrophosphate and metaphosphate of silver, this should appear on partial precipitation, for instance on employing an excess of the soda salt, and the precipitate obtained in such a manner should exhibit the composition of pyrophosphate of silver. On the other hand, upon adding an excess of nitrate of silver to the filtered solution, a precipitate should be obtained which should approach in composition to the metaphosphate of silver. But the following analyses of the silver precipitates, prepared with attention to these circumstances, showed that such a partition does not take place. The salt of magnesia afforded the same result; metaphosphate of soda produces no precipitate in a solution of sulphate of magnesia. If any partition occurred, the precipitate obtained with the latter salt should possess the composition of the pyrophosphate of magnesia.

The Silver Salt, $6AgO, 4PO^5$ (fused), is obtained by precipitating nitrate of silver with the soda salt; the precipitate must not be washed too long, otherwise it loses phosphoric acid. When dried at 212° the silver salt contains but little water; at a somewhat higher temperature it fuses, and was employed in this state for analysis. The precipitates I. and II., which were prepared with an excess of the soda salt, furnished, owing to an admixture of ordinary phosphate of soda, too large an amount of silver, which was not the case when an excess of the nitrate of silver was employed. I. furnished

72·39, II. 72·39, III. 70·50, IV. 70·56, V. 71·09 per cent. of oxide of silver. Calculation requires—

AgO	6 =	696	70·73
PO^5	4	288	29·27

The Magnesia Salt, $6MgO, 4PO^5$, *the Baryta Salt*, $6BaO, 4PO^5$, and *the Lime Salt*, $6CaO, 4PO^5$ (heated), are obtained by precipitating sulphate of magnesia, chloride of barium and chloride of calcium with the soda salt. They are all three infusible, and when heated higher than requisite to deprive them of their water, are rendered insoluble in acids. The salts of the alkaline earths belonging to this series are very easily prepared by fusing any of their soluble salts with the soda salt; they are left as heavy crystalline powders on exhaustion with water.

Berzelius has already described a silver salt, $3AgO + 2PO^5$, and a baryta salt, $3BaO + 2PO^5$, and assigned to them the name sesquiphosphates. These salts are identical with those enumerated by the authors in this last series (with the equivalents doubled). As the phosphoric acid in these salts requires a separate name, the authors propose that of sesquiphosphoric acid. With respect to its reactions, it must be arranged between the metaphosphoric and the pyrophosphoric acids; from the latter it differs by its silver salt being soluble in a very large excess of the soda salt, and from the former by the insolubility of its magnesia salt.

The Soda Salt of the second of the above-mentioned members, $6NaO + 5PO^5$, was obtained by fusing together 100 parts by weight of pyrophosphate of soda and 307·5 metaphosphate (fused, according to Graham). This soda salt furnishes with a solution of silver a precipitate which is readily soluble in an excess of the soda salt, and possesses the formula $6AgO + 5PO^5$ (fused).—Liebig's *Annalen*, lxv. p. 304.

Mesoxalates of Lime and Baryta.

L. Svanberg and I. Kolmodin have examined two earthy salts of mesoxalic acid, viz. the baryta salt, $BaO, C^3 O^4$, which separates in laminar crystals, and is rendered anhydrous at 194°. The salt was burnt, and it was completely confirmed that the acid contains no hydrogen. It begins to be decomposed at 212°, but the decomposition is not complete at that temperature.

The lime salt, $CaO, C^3 O^4 + 2HO$, which is far more soluble than the preceding, crystallizes in thin prisms. After desiccation at 194°, it retains the 2 atoms of water, one of which is however expelled at 284°. Above that temperature it begins to be decomposed, and cakes together.—Liebig's *Annalen*, lxiv. p. 308.

On Quinoidine. By F. Roder.

The author has, in consequence of the results published by Liebig on the constitution of quinoidine, made some experiments to obtain from quinoidine or amorphous quinine the latter in a crystalline state. 1 part of commercial quinoidine is dissolved in 4 parts alcohol

of 0·865, and a solution of $\frac{1}{2}$ a part protochloride of tin in 2 parts of water added to it. This precipitates a dark resinous mass, while the supernatant liquid is but faintly coloured; it is separated from the precipitate, and quickly precipitated with ammonia. The precipitate is then well-washed and dried, and exhausted with alcohol as long as this removes anything; the united extracts are again mixed with half the former amount of protochloride of tin, again quickly precipitated with ammonia, and the well-washed and dried precipitate exhausted with alcohol, when an almost colourless solution of pure quinine is obtained, which, carefully saturated with dilute sulphuric acid, affords on evaporation crystals of sulphate of quinine.

In the liquid filtered from the precipitate of protoxide of tin and quinine, as well as in the wash-water, cinchonine is contained if ordinary quinoidine has been employed which has not been previously purified by precipitation with an alkali. These liquids, containing cinchonine, are precipitated with tincture of galls to obtain the cinchonine in the usual manner.

The precipitated resinous substance still retains some quinine, to obtain which it is dissolved in alcohol, again mixed with a strong solution of protochloride of tin, and then further treated in the above-mentioned manner. The resinous substance so obtained is of an alkaline nature, of a bitter taste, and possesses the peculiar odour of quinoidine; it would probably yield more quinine on further treatment.

The author obtained by this process from two different samples of quinoidine, in one case 43 per cent. quinine, 9 per cent. cinchonine and 28 per cent. resin; and in the second 40 per cent. quinine, 10 per cent. cinchonine and 30 per cent. resin; the water amounted to 20 per cent. On precipitating 100 parts of commercial quinoidine in solution with an alkali, the precipitate obtained weighed 69 grs. —*Mittheilungen des Schweizer. Apothekervereins*, vol. i. p. 31.

On the so-called Hydrate of Oil of Turpentine. By Dr. C. List.

This substance, which has been analysed by several chemists with the same results, is represented by the formula $C^{20}H^{22}O^{6}$, and may consequently be looked upon as a hydrate of the oil of turpentine; but as it is evident from its properties, and especially from the reactions noticed by the author, that this view of its constitution has just as little claims to correctness as the corresponding one with respect to alcohol, its name had consequently to be altered, and the author adopts that of *terpine*, proposed for it by Berzelius.

The material employed by the author in his experiments was prepared according to the process described by Wiggers*, by leaving oil of turpentine for a long time in contact with a mixture of nitric acid and alcohol; in the course of some months more than a pound was obtained. The crystals of terpine are orthorhombic prisms; they melt when heated with loss of water, and the anhydrous compound then solidifies to a milk-white crystalline mass, which very rapidly

* Chem. Gaz., vol. iv. p. 364.

reabsorbs water from the atmosphere, expanding at the same time considerably. The loss of water on fusion amounts to 2 atoms or 9·464 per cent.; it also takes place at the ordinary temperature over sulphuric acid. Anhydrous terpine, $C^{20} H^{20} O^4$, melts at 217° F., and solidifies at 196°. If cooled very quickly, it remains soft and amorphous, but again passes into the crystalline state by contact, heat or moisture. It sublimes in long shining prisms when heated above its melting-point; but a constant current of air is requisite for this, and it does not take place in a close vessel.

By a remarkable action of acids, 3 equivs. oxygen and 3 equivs. hydrogen may be separated in the form of water from the constitution of terpine; the new product thus produced belongs from its properties to the class of essential oils; the author proposes for it the name of *terpinole*. According to the analysis made with it, its composition is represented by the formula $C^{28} H^{17} O$. It might, therefore, according to the former view, be regarded as the first hydrate of the oil of turpentine. It is produced by the action of the most different, even of the weakest acids upon terpine. When a few drops of an acid are mixed with a hot solution of terpine in water, and the whole is then heated nearly to boiling, a milkiness results, and the liquid at the same time acquires a most agreeable odour; and when submitted to distillation, the whole of the terpine passes over with the water in the form of oily terpinole. One drop of sulphuric acid sufficed to turn a whole ounce of terpine into terpinole.

Terpinole is a colourless, very liquid oil, with the agreeable odour of hyacinths; its specific gravity is 0·852, and its boiling-point 334°. All attempts to reconvert it into terpine by treating it with alkaline liquids, or by keeping it for a length of time at 334° in contact with water, proved unsuccessful.

The production of terpinole appears to result from a catalytic action; the acid seems to act merely by contact; it remains unaltered, and extends its action to apparently unlimited quantities of terpine. The author however is not inclined to adopt this view, but considers it probable that this metamorphosis depends on the previous production of a very unstable acid body, as in the production of æther from sulphovinic acid. He did not succeed, it is true, in obtaining any such supposed combination with an oxyacid; but the behaviour of hydrochloric acid is in favour of this view. When this acid is passed in a gaseous state into terpine powder, it is absorbed with evolution of heat and liquefaction. On cooling, the mass, perfectly saturated with gas, solidifies from the separation of crystalline laminæ, which were obtained pure by pressure and recrystallization from cold alcohol. This body crystallizes in large shining laminæ; it melts at 122°, has a peculiar odour, and is composed according to the formula $C^{20} H^{18} Cl^2$; it might therefore also be regarded as $C^{20} H^{17} Cl + HCl$. In fact, when heated with water or alcohol, it is entirely converted into hydrochloric acid and terpinole, just as if it contained the chlorine compound corresponding to terpinole. This view is moreover supported by the fact, that it can be produced

just as readily from terpinole as from terpine, by saturating it with muriatic gas. It is isomeric with the crystalline muriatic compound of the oil of lemons, but decidedly distinct in its properties. No similar iodine compound could be obtained. When terpine is heated with concentrated hydriodic acid, it is converted into terpinole.

When terpine is distilled with anhydrous phosphoric acid, the whole of the oxygen is removed in the form of water, and the residue is an oil having the same per-centage composition as the oil of turpentine.—*Journ. für Prakt. Chem.*, vol. xliii. p. 499.

On the Occurrence of Vanadium in the Refinery Slag of Staffordshire. By Isaiah Deck.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—Being commissioned by an eminent English railway engineer, who has directed much attention towards the qualities of iron employed in bridges, &c., to examine some refinery slag, which, without any assignable reason, had the property of imparting extraordinary ductility to the iron with which it was mixed, I have succeeded in discovering a large quantity of vanadium, existing as silicate of vanadic acid, combined with small portions of molybdena, chrome, and the usual quantities of phosphoric acid and silicates. The first metal being confined to few localities, has had its properties but little studied by English chemists, and has hitherto been found in no other slag than that from the Taberg mine in Sweden, the iron of which is remarkable for its ductility; and no mention is made of it in the elaborate analyses of slags by Dr. Percy, performed for the British Association, and published in vol. v. p. 293 of the 'Chemical Gazette.'

The quantity of slag at my command operated upon was very small; but the vanadium existed in a much larger proportion than in the Swedish slag, which I have since examined; and it is doubtless the cause of the superior ductility of both. In a short time I shall be enabled to lay before your readers the results of examination of a large quantity of the slag, as at present the analysis is the private property of the party employing me.

The *entire* merit of the discovery does not rest with myself; and I am happy in this notice to bear testimony to the suggestions and superintendence of Professor Wöhler, in whose well-appointed laboratory the analysis was performed.

Göttingen, July 17, 1848.

Observations on Lactic Acid. By H. Engelhardt.

Liebig, in his memoir on the constituents of the fluids of flesh, has already drawn attention to the circumstance that the amount of water of the zinc and lime salts of the lactic acid which occurs in the fluids of the flesh differs from that contained in the same salts prepared with lactic acid obtained by the fermentation of sugar.

The salts of the latter acid were some time ago examined by the author in conjunction with Maddrel*. The peculiarity above mentioned has induced the author to compare the acid from the fluids of the flesh with that obtained from sugar; and he has arrived at the result that most probably two isomeric compounds of the formula $C^6 H^5 O^5$ exist, or that the lactic acid may occur both monobasic and bibasic. For the present the author distinguishes the acid from the fluids of the flesh by the name of *a* lactic acid from the *b* lactic acid prepared from sugar.

Properties of the two Acids.—In the free state, as far as it has yet been possible to examine them, they present no difference; both are very readily soluble in alcohol, æther and water, and do not crystallize. They are separated from the zinc salt by sulphuretted hydrogen. Their soda salts behave quite similarly towards solvents, and in both the zinc salt is formed in the same manner and with the same physical properties.

The difference of the two acids will be seen from the following analyses of some salts:—

Lime Salt.—The salt of the *a* lactic acid contains, when crystallized from water, constantly 4 atoms, that of the *b* lactic acid 5 atoms of water; but the behaviour of the two acids towards alcohol is quite unusual. If, for instance, the lime salts are crystallized from alcohol, they both combine with 5 atoms of water; and when these salts are subsequently recrystallized from water, the lime salt of the *b* lactic acid alone retains its 5 atoms of water, while the *a* lactic acid takes up only 4. By drying at 212°, the salt of the acid *b* parts with its water far more quickly than that of the acid *a*. Both lime salts dissolve in boiling water and alcohol in every proportion; but the salt of the acid *a* requires 12·4 parts of cold water for solution, while that of the acid *b* requires only 9·5 parts. The physical properties agree in every respect, and nothing characteristic could be observed in the grouping of the crystals. The following are the results of the analysis:—

Salt of the a *Lactic Acid.*—Amount of water in the salt crystallized from water on cooling:—

I.	1·3440 grm.	substance lost at 212°	0·3540	water =	26·339 per cent.
II.	0·7115	... ...	0·1170	...	24·877 ...
III.	0·8135	... ...	0·2025	...	24·892 ...
IV.	0·8150	... ...	0·2115	...	25·939 ...
V.	0·4990	... ..	0·1270	...	25·451 ...

Salt crystallized from water by spontaneous evaporation:—

VI.	0·6395 grm.	substance lost at 212°	0·1635	water =	25·566 per cent.

Salt crystallized from boiling alcohol by cooling:—

VII.	0·8070 grm.	substance lost at 212°	0·2335	water =	28·933 p. c.
VIII.	0·5680	... ...	0·1650	...	29·049 ...

The *lime* was estimated in the dry way by converting the salt into

* Chem. Gaz., vol. v. p. 484.

sulphate of lime. The same appearances occurred on ignition as with the salt of the *b* lactic acid—a considerable tumescence, with a very characteristic odour:—

I. 0·5715 grm. subst. III. yielded 0·350 CaO, SO^3 = 25·214 p.c. CaO.
II. 0·4650 ... V. ... 0·288 ... 25·506 ...

Salt of the b *Lactic Acid.*—The amount of water in the salt crystallized from water by cooling:—

I. 0·920 grm. lost at 212° 0·262 water = 28·478 per cent.

Salt crystallized from water by spontaneous evaporation:—

II. 4·4295 grm. lost at 212° 0·294 water = 29·230 per cent.

Salt crystallized from alcohol by cooling:—

III. 1·068 grm. lost at 212° 0·313 water = 29·300 per cent.

5 equivs. water require 29·220 per cent.
4 ... ... 24·828 ...

The anhydrous salt contains 25·688 per cent. lime.

Magnesia Salt.—The salt of the *a* lactic acid is much easier soluble in water and alcohol than that of the *b* lactic acid; the former contains 4 equivs. water, the latter only 3, and also differs in external appearance.

Zinc Salt.—That of the *a* lactic acid always combines with 2, that of *b* lactic acid constantly with 3 equivs. water. Besides this difference in the amount of water, the salts likewise exhibit a considerable difference in the manner in which they part with it. While, for instance, the salt of the *b* lactic acid soon gives off its water at 212°, that of the *a* lactic acid requires several hours (in one case nine hours) before its weight is constant. The salt of the *b* lactic acid may moreover be heated up to 400° without being decomposed. That of the *a* lactic acid experienced between 212° and 302°, at which temperature it was kept but for a short time, a loss of 1·157 per cent., and the vessel in which it was contained had an empyreumatic odour. The salt of the *a* lactic acid dissolves in 2·88 parts boiling and 5·7 of cold water; in 2·23 parts of cold and in nearly as much boiling alcohol. For this reason Liebig used the lime salt instead of the zinc salt to prepare the lactic acid from the fluids of the flesh. The salt of the *b* lactic acid dissolves in 6 parts of boiling and 58 parts of cold water, and is almost insoluble in alcohol. The salt of the *a* lactic acid is deposited on the cooling of the solution in dull, irregularly-grouped, extremely thin needles, which fall to a crystalline paste as soon as the vessel is touched. The crystalline masses of the salt of the *b* lactic acid usually have considerable lustre, form crusts, and very rarely a confused aggregate of acicular crystals.

The author found in the zinc salt of the acid *a* 12·895 and 13·430 per cent. of water and 33·333 per cent. oxide of zinc. The formula $ZnO, C^6 H^5 O^5 + 2HO$ requires 12·901 per cent. water and 33·349 oxide of zinc.

Nickel Salt.—The salt of the *a* lactic acid loses the third equiva-

lent of water at 212°; the salt of the *b* lactic acid does not part with the third equivalent before 266°.

Copper Salt.—In this salt the difference between the two acids is very perceptible; the salt of the *a* lactic acid crystallizes from water in small, hard, dull sky-blue, warty masses, while that of the *b* lactic acid separates in tolerably large perfect crystals of considerable lustre and of a dark blue or greenish colour. With respect to solubility the salts differ very considerably; the latter dissolves in 6 parts of cold and 2·2 of boiling water, in 115 cold and 26 parts boiling alcohol; the former in 1·95 parts of cold, in 1·24 parts of boiling water, and far more readily in alcohol. The amount of water of crystallization, the behaviour over sulphuric acid at 212° and at a higher temperature, are likewise very different. The salt of the *b* lactic acid contains 2 equivs. water, which are very soon expelled over sulphuric acid without its appearance being altered; this is likewise the case when it is exposed to a temperature of 212°. It is decomposed between 392° and 400°, at which temperature it takes fire and burns away like tinder, leaving a residue of metallic copper. Below this temperature it may be retained for any length of time without its appearance being in the least altered. It dissolves readily and entirely in water, &c. From the following analysis the amount of the water contained in the salt of the acid *a* cannot be determined with certainty. For instance, the salt had lost but a very small portion after being kept for several weeks over sulphuric acid; it had caked together, and had changed its blue into a brownish colour. At 212° this sample acquired a greenish colour; the salt not previously dried over sulphuric acid behaves precisely in the same manner at this temperature. When the salt had been dried so long at 212° that no decrease in weight was perceptible, a further considerable loss resulted at 284°. If now heated in the water-bath, a considerable quantity of red protoxide of copper is left. None of these phænomena are exhibited by the copper salt of the *b* lactic acid.

The copper salt of the *a* lactic acid lost at 212°, changing its colour but not caking together, 8·956–9·581 per cent. water; but it had to be kept for several hours at this temperature; these quantities however do not correspond to any simple atomic proportion. The salt, which had lost 8·956 per cent. water, left 32·866 per cent. oxide of copper; calculation requires 32·91.

What has been communicated led the author to conclude that the lactic acid produced by fermentation from sugar is distinct from that contained in the fluids of the flesh. The latter however is probably identical with that in sauerkraut, for Liebig states, in his 'Manual of Chemistry,' p. 816, that the neutral zinc salt (of lactic acid prepared from sauerkraut), when dissolved in water and mixed with alcohol, separates into a basic and acid salt. The author endeavoured in vain to prepare the basic salt with the lactic acid from sugar; the neutral salt was boiled for several days with carbonate of zinc, oxide of zinc, and hydrated oxide of zinc; when it was treated with potash, ammonia or hydrate of baryta, a precipitate resulted which was not

diminished by continued boiling, and was not decomposed by treatment with alcohol either in the cold or on the application of heat; only the neutral salt could be obtained.

The author is still occupied in examining the salts of the *b* lactic acid. He states, that on the dry distillation of the lactate of copper, he obtained different results from those found by Pelouze, viz. aldehyde, a new acid and unaltered lactic acid.—Liebig's *Annalen*, lxv. p. 359.

On the Occurrence of Berberine in the Root of the Barberry and Columbo. *By* Dr. C. Bödeker.

The root of *Cocculus palmatus*, which has long been exported under the name of Columbo root from the East Indies for therapeutical purposes, contains, as is well known, a non-nitrogenous substance, columbine, which has hitherto been little examined, and which the author had selected as a fit subject for investigation. In the preparation of this substance he found along with the colourless crystals of columbine some beautiful golden crystals, which dissolved readily in hot lime-water with a dark red colour, from which solution they separated on the addition of an excess of hydrochloric acid in light golden yellow needles, which easily dissolve in pure water. From the behaviour of this solution it was evident that the crystals were the chlorine compound of an organic base. On this account the substance in question was prepared in larger quantity in the following manner:—The Columbo root was exhausted with hot alcohol of 0·889, as much of the alcohol as possible removed by distillation; and when a yellowish-brown mass of impure columbine had separated after three days' standing, the supernatant liquid, together with the aqueous solution arising from the rinsing of the impure columbine, was evaporated to dryness in the water-bath. The residue was exhausted with boiling alcohol of 0·863 spec. grav., and this solution again treated as the preceding one. The residue was then treated with boiling water, and the filtered solution mixed with a considerable quantity of muriatic acid. The precipitate thus formed was collected on a filter and well pressed between paper. Owing to its great solubility in pure water and alcohol, it could not be washed. To remove any free adherent acid, it was dissolved in alcohol of 0·863, and precipitated from this solution by æther. The salt so obtained was an indistinctly crystalline bright yellow powder of a disagreeable bitter taste. An aqueous solution of it furnished yellow amorphous precipitates with chloride of platinum, perchloride of mercury, tannic acid, chlorate and chromate of potash. The dry salt disengaged ammonia when heated with soda lime, but the aqueous solution afforded no ammonia when treated with potash.

All these properties indicated that the organic base combined with hydrochloric acid must either be berberine or one very similar to it. Several careful analyses, the results of which agree with the known composition of berberine, have proved that this substance is really berberine, and that consequently the same organic base is

produced in the root of the European *Berberis* and the root of the East Indian *Cocculus*.

This circumstance merits attention in a therapeutical point of view, since the berberine is present to a large amount in the Columbo root, and indeed to a much greater extent than the columbine. While the latter is almost insoluble in water and but sparingly soluble in cold alcohol, berberine is abundantly dissolved by hot water and by alcohol; so that in using an aqueous extract of Columbo, besides starch, berberine alone can be looked upon as the essential principle.

This occurrence of berberine in *Berberis* and *Cocculus* is also interesting in a botanical point of view. The true alkaloids, with the exception of caffeine, which however likewise differs from them in its behaviour, exhibit in their distribution a relation with the natural affinities of the plants. The views of botanists respecting the correct systematic position of the *Berberideæ* are still divided. Bartling arranges them with *Menispermeæ*, to which *Cocculus* belongs, and forms of these two families the class *Cocculinæ*. The production of the same peculiar vegetable principle in plants of the two families supports this view.

The peculiar vegetable principles to which the alkaloids belong are said nearly all to occur in the so-called laticiferous vessels, and never in the cells of the plant. A microscopic examination of the roots of *Cocculus palmatus* and *Berberis vulgaris* showed however that in both the berberine is deposited in the thickening layers of cellular membrane.

With respect to columbine, the small quantity procured by the author did not admit of his arriving at perfectly satisfactory results as to its composition. The mean of two analyses led to the formula $C^{14} H^{8} O^{5}$.

From the mode of occurrence of columbine in the Columbo root it is probable that its production in the vegetable organism precedes that of the berberine, as the columbine is found only in the exterior and younger parts of the parenchymatous tissue, while scarcely any is observed where vascular bundles are developed.

If we suppose that the base has been formed from the non-nitrogenous body by the action of ammonia, a remarkable relation is evident between columbine and berberine on the one hand and picrotoxine and menispermine on the other. The basic menispermine occurs in the shells of the fruit of *Anamirta cocculus* which are exposed to the reducing action of sunlight; the picrotoxine is met with in the kernels. While in the present instance the formation of the base from the non-nitrogenous body is connected with a process of deoxidation, in the case of the root of *Cocculus palmatus* which is protected from the sunlight it is connected with a process of oxidation.

When 3 equivs. of oxygen are added to 3 equivs. columbine and 1 equiv. ammonia, and 9 equivs. water removed, the composition of berberine is obtained. The author is at present engaged with experiments in this direction.—*Journ. für Prakt. Chem.*, vol. xliv. p. 501.

On the Combinations of Strychnine and Brucine with Ferro- and Ferridcyanogen. By D. BRANDIS.

The author has succeeded in preparing the two double cyanides of strychnine and brucine corresponding to the yellow and the red prussiates of potash. The formulæ adopted have been obtained from numerous accordant analyses. The author adopts for strychnine the formula $C^{44}H^{24}N^2O^4$, and for brucine the formula $C^{46}H^{26}N^2O^8$.

Ferrocyanide of Strychnine, (2StrHCy + FeCy) + 8HO, is formed when the solution of a perfectly neutral salt of strychnine and the solution of ferrocyanide of potassium, both cold and saturated, are mixed with each other; the compound immediately separates in the form of a precipitate consisting of nearly colourless acicular crystals. On employing dilute solutions, the crystals may be obtained more than an inch in length; they are rectangular four-sided prisms, of a pale yellow colour, sparingly soluble in cold water and alcohol, and more soluble in hot. At 212° the salt loses 6 equivs. water = 6·12 per cent., and then immediately begins to be decomposed with evolution of prussic acid. It behaves like the ferrocyanide of potassium towards salts of iron, copper and lead. When its solution is heated to boiling, it acquires a dark yellow colour, with the separation of crystalline strychnine, and then ferridcyanide of strychnine crystallizes from the solution.

Ferridcyanide of Strychnine, (3StrHCy + Fe^2Cy^3) + 12HO, is obtained in the manner just mentioned, or by mixing a hot saturated solution of a salt of strychnine and ferridcyanide of potassium, likewise by boiling strychnine with prussian blue and water; it forms minute, very sparingly soluble prisms of great lustre and a golden colour. It loses 3 equivs. water over sulphuric acid *in vacuo*, 6 equivs. at 212°, and 8 equivs. at 277°; it then begins to be decomposed and to turn green, and at 392° it becomes black; its solution is only partially decomposed by long-continued ebullition. It furnishes prussian blue with protosalts of iron. Potash and ammonia decompose it with separation of crystalline strychnine.

A very remarkable compound, corresponding to the formula (StrHCy + HCy + 2FeCy) + 5HO, is obtained when a solution of ferrocyanic acid in alcohol is added to a solution of strychnine in alcohol. It separates in the form of a white pulverulent precipitate, is perfectly amorphous, nearly insoluble in alcohol and water, and has a strong acid reaction; it parts with 2 equivs. water below 212°, at which temperature it is decomposed with a lively disengagement of prussic acid. By long contact with water, and especially when heated, it is decomposed, with the separation of a blue precipitate, evolution of prussic acid, and formation of the ferridcyanide of strychnine.

It is difficult to say what view should be taken of the constitution of this body. It might be looked upon as an analogous compound to the ferrocyanic acid = (StrHCy + 2FeCy) + HCy, which should furnish with bases so-called triple cyanides. The experiments made on this point showed that if, as was probable, such compounds were

produced, they at all events were very quickly decomposed. Mixed with an alcoholic solution of strychnine, it is converted into crystalline ferrocyanide of strychnine, but which even at the ordinary temperature quickly passes into the ferridcyanide, with separation of a blue amorphous substance.

Ferrocyanide of Brucine, (2BruHCy + FeCy) + 2HO, closely resembles the corresponding compound of strychnine; but it differs from it in this respect, that when heated with water a blue precipitate is separated without the production of the ferridcyanide.

The Ferridcyanide of Brucine is likewise perfectly similar to the corresponding salt of strychnine.

Muriate of Strychnine and Cyanide of Mercury, StrHCy + 4HgCy. —This compound is formed when a solution of muriate of strychnine is mixed with one of cyanide of mercury. According to the degree of concentration or temperature, the compound separates either immediately or at a later period; it forms colourless, rectangular, four-sided prisms, with a lustre of mother-of-pearl. Some experiments upon animals show that it is one of the most violent poisons.—*Journ. für Prakt. Chem.*, p. 505, May 15, 1848.

Observations on Cystine. By M. Berzelius.

This substance, which is so rarely met with in urinary calculi, was discovered by Wollaston, who called it cystic oxide. From the description which he has given, it constitutes an organic base, yielding neutral salts with acids. The experiments of Wollaston are quite sufficient to decide the question; but the organic bases were not known at the period when he discovered this body, otherwise he would not have hesitated to place it in that class. The name oxide indicates, in fact, that he attributed to it basic properties. The composition of this substance should be represented by the formula $NH^3 + C^6 H^5 S^2 O^4$. To confirm this view, I dissolved some well-determined crystals of the ammonio-chloride of cystine in water, and then added a suitable quantity of neutral chloride of platinum, and left the mixture to spontaneous evaporation. The double salt is extremely soluble, and on drying forms an amorphous mass of a beautiful orange colour, which does not present a trace of crystallization, and dissolves in water and in absolute alcohol. It is insoluble in æther, but this latter does not precipitate it from the alcoholic solution.—Berzelius's *Jahresbericht* for 1848, p. 376.

Researches on the Protochloride of Arsenic and some Arsenites. By L. Pasteur.

Action of dry Ammoniacal Gas upon the Protochloride of Arsenic. —When dry ammoniacal gas is passed into a balloon containing protochloride of arsenic, the temperature of the chloride rises, and it becomes converted into a white, pulverulent, amorphous substance, which is inodorous, and when saturated with ammoniacal gas possesses, according to H. Rose, the composition $2AsCl^3 + 7NH^3$. The author is of opinion that a similar reaction takes place between

the ammoniacal gas and the protochloride of arsenic, as occurs in the case of protochloride of phosphorus and ammonia, that is to say a mixture of chloride of ammonium and of *chlorarsenimide* is produced. Taking Rose's formula for the direct product, we have in fact

$$2AsCl^3 + 7NH^3 = 2(ClAsNH) + 4(ClNH^4) + NH^3.$$

One fact in favour of this opinion is, that if the substance is heated in a tube, at first a large quantity of ammonia is disengaged, and the whole of the substance then sublimes; but, according to M. Pasteur, a number of minute cubic crystals of chloride of ammonium are very easily detected, especially in the portions last sublimed. What first sublimes is a mixture of chlorarsenimide and chloride of ammonium. The difference in volatility of these substances is not sufficient to allow of isolating by this means the chlorarsenimide in a state of perfect purity.

Boiling water completely destroys the ammoniacal protochloride of arsenic, giving rise to a disengagement of ammonia, while arsenious acid and chloride of ammonium remain in solution or are precipitated. Water of the ordinary temperature, or somewhat warmed, causes the mass to evolve heat at the same time that ammonia is disengaged. The liquid, allowed to cool, deposits on spontaneous evaporation a crystalline mass, which adheres strongly to the sides of the vessel, and is composed of very beautiful, regular, hexagonal tables. The author found it to contain,—chlorine, 13·43; arsenic, 58·10; nitrogen, 5·35; hydrogen, 2·30; and oxygen, by loss, 20·82 per cent. These numbers correspond to the formula $ClAs^2NH^5O^7_2$*. The following is the reaction which gives rise to this compound. When the ammoniacal protochloride of arsenic is treated with water, NH^3 is dissolved or partly disengaged, as is evident from the odour; the chloride of ammonium dissolves, and 2(ClAsNH) assimilate the elements of 7 equivs. water to form the new compound; at the same time another equiv. of chloride of ammonium enters into solution—

$$2(ClAsNH) + \tfrac{7}{2}OH^2 = ClAs^2NH^5O^7_2 + ClNH^4.$$

The new compound contains the elements of chlorarsenimide, arsenious acid and water:—

$$ClAs^2NH^5O^7_2 = ClAsNH + \tfrac{1}{2}As^2O^3 + 2OH^2.$$

It may also be regarded as a biarsenite of ammonia, in which a part of the oxygen is replaced by chlorine, $As^2O^7_2Cl\,(H, NH^4)$, similar to $As^2O^4\,(H, NH^4)$. But whatever be the case, if the new compound is treated with concentrated ammonia, it at once solidifies to a hard mass, which adheres to the vessel, and is composed of elongated hexagonal tables grouped together, and containing $As^2O^4\,(H^2, 2NH^3)$. It is therefore the neutral arsenite of ammonia. This salt is very unstable when separated from water charged with ammonia; its solution in water diffuses a strong odour of ammonia, and it is gradually destroyed. Exposed to the air in the solid state, it loses every trace of ammonia in the course of a day, leaving pulverulent arsenious acid.

* Gerhardt's notation.

Arsenite of Ammonia.—When concentrated ammonia is poured over arsenious acid, it solidifies to a hard mass, which adheres strongly to the sides of the vessel; at the same time there is a very perceptible elevation of temperature. This mass is nothing less than crystallized arsenite of ammonia. The form of this salt is that of an oblique prism with a rectangular base. This salt gives with nitrate of silver a bright yellow precipitate, containing $As^2 O^4 (Ag^2)$, $O (Ag^2)$, and no water of crystallization. The supernatant liquid is acid, and the precipitate gradually disappears, being soluble in acid liquids.

The author has not succeeded in obtaining an arsenite of ammonia corresponding in composition to that of the preceding silver salt.

Arsenites of Potash.—There are several arsenites of potash. When a cold solution of potash is mixed with an excess of arsenious acid, the temperature gradually rises, and an oily liquid is obtained, which does not crystallize, and which affords with nitrate of silver a yellow precipitate provided the solutions are dilute. The precipitate is more or less white according as more or less arsenious acid is precipitated with it. In every case the supernatant liquid acquires a decided acid reaction. The acidity which the liquid, at first strongly alkaline, acquires, and the simultaneous precipitation of a considerable quantity of arsenious acid, admits of the conclusion, that the arsenite formed is an acid arsenite. This is confirmed by experiment; in fact, if the filtered liquid obtained by saturating potash in the cold with arsenious acid is treated with alcohol, it becomes viscid, and may be drawn out into threads like a thickened oil, rendered opake and white by the interposition of a number of globules of alcohol, which gradually disappear when the liquid is set aside for a couple of days. The sides of the vessel are then found to be coated with a multitude of very beautiful right rectangular prismatic crystals. In the course of some days the whole of the syrupy mass has become solid. These crystals contain, according to the author, $As^2 O^4, (KH) + \frac{1}{2}aq.$ The $\frac{1}{2}aq.$ is expelled at 212°.

If the preceding salt is mixed with carbonate of potash, and the liquid then boiled for several hours, carbonic acid is disengaged, and a product is formed which is very sparingly soluble in alcohol. When agitated several times with this liquid, a syrupy substance is obtained, which contains $As^2 O^4 (K^2)$; it is the neutral arsenite of potash.

If to the solution of acid arsenite an excess of caustic potash is added, and the viscid liquid now precipitated by alcohol, the whole excess of potash is removed, and there remains a product very soluble in water, the composition of which corresponds to the yellow silver salt, viz. $As^2 O^4 (K^2), O (K^2)$; it is consequently a subsalt like the latter; and, in fact, on precipitating it with nitrate of silver, yellow arsenite of silver is obtained, however dilute or concentrated the liquids; but now the yellow precipitate is persistent, and the supernatant liquid is perfectly neutral to test-paper if care has been taken to add an excess of nitrate of silver.

The author is also inclined to believe that a fourth arsenite of

potash exists, but which is soon decomposed in the presence of water.

Arsenites of Soda.—What has been above stated with respect to the arsenites of potash applies equally to the arsenites of soda. M. Pasteur obtained three arsenites of this latter metal, but the acid salt is not crystallizable like the corresponding salt of potash.

Isomorphism and Dimorphism of the Hydrated Arsenious and Antimonious Acids.—When a boiling solution of potash is saturated with arsenious acid, a very syrupy liquid is obtained, which dissolves entirely in water, forming a true combination, but which is gradually destroyed by the presence of this very water, depositing a large amount of arsenious acid. If the amount of water added is not too considerable, this deposit is always obtained coating the sides of the vessel; but what is most remarkable is, that the arsenious acid deposited under these circumstances has never, or but very seldom, the form of a regular octahedron. M. Pasteur has frequently repeated this experiment, and only in one case did he obtain octahedral arsenious acid. The acid obtained by this method assumed various forms, all of which may be referred to a rectangular prism with a rhombic base.

The exitele of mineralogists (oxide of antimony or antimonious acid) is completely isomorphous with this last variety of arsenious acid. One of the most prominent characters of the native oxide of antimony is its adamantine, nacreous, silky lustre; the prismatic arsenious acid presents exactly the same appearance. This striking analogy of form led the author to attempt to produce antimonious acid crystallized in regular octahedrons, and he succeeded in the following manner:—Algaroth powder, recently precipitated and washed with an excess of carbonate of soda, was digested for several days; a yellowish oxide was thus obtained in the form of a granular crystalline powder, which under the microscope consisted of an infinite number of minute octahedral crystals, not to be distinguished from the octahedral arsenious acid; they were, moreover, mixed with other prismatic crystals, possessing exactly the form of the arsenious acid with the same modifications. These two oxides are consequently at the same time dimorphous and isomorphous, or, in the language of mineralogists, isodimorphous.—*Journ. de Pharm.*, May, 1848, p. 395.

Chromate of Potash and Arsenious Acid.

Schweitzer states, that when a solution of arsenious acid is added to a solution of neutral chromate of potash, the liquid acquires a beautiful green colour, and in a few minutes congeals to a trembling jelly, the empirical formula of which, after desiccation at 212°, is $3AsO^5 + 4KO + 3Cr^2O^3 + 10$ aq. If the liquids are added in the reverse order, a green colour is produced, but no precipitate.—*Journ. für Prakt. Chem.*, vol. xxxix. p. 267.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Discovery of a new Organic Base in Opium.

By Dr. G. Merck.

Opium appears to continue an inexhaustible source of new substances, and especially of such as possess basic properties. Up to the present time five such bodies have been prepared from opium and satisfactorily proved to be distinct; and I have now succeeded in discovering a new base in the residues from the preparation of morphium, which I shall call *papaverine*. I shall at present merely establish the peculiarity and formula of this body, and shall on a future occasion describe more fully its preparation, its reactions, and its medicinal properties, if it possess any.

The pure base separates from alcohol in confused aggregations of white acicular crystals, and from æther in somewhat larger needles. It is very sparingly soluble in cold, more soluble in boiling alcohol, from which it again separates in a crystalline state on cooling; it is likewise very sparingly soluble in cold æther, and is deposited in crystals from a boiling ætherial solution on cooling. It is insoluble in water. The solution scarcely turns red litmus-paper blue. When the crystals are moistened with concentrated sulphuric acid, they turn blue.

Papaverine forms with acids salts, the majority of which are very sparingly soluble in water, the muriate being especially characterized by the ease with which it crystallizes. The base dissolves readily in moderately concentrated muriatic acid; and on the addition of more acid a white precipitate first separates, which collects into drops, and forms an insoluble oily layer at the bottom of the vessel. When left quiet, crystals form in the oily and likewise in the supernatant aqueous liquid, which continue to increase for a long time until the entire mass of the oily liquid is converted into a tissue of well-defined crystals several lines in length. A gentle heat facilitates the crystallization. The oily liquid dissolves on boiling, and again separates for the greater part on cooling. When some crystals, freed by washing with water from adherent acid, are dissolved in water, the solution remains transparent on cooling, and only after several days' standing do large crystals separate; when, on the con-

trary, a little muriatic acid is added to the cold solution, the salt separates in the above-described form. The crystals of the muriate are very sparingly soluble in cold water; the solution has no action upon litmus-paper. The muriate of papaverine crystallizes in right rhombic prisms.

Sulphuric and nitric acids behave towards the base like muriatic acid, only the crystals could not be obtained of such large size.

With chloride of platinum the muriate of papaverine yields a yellow precipitate, which is insoluble in boiling water and in boiling alcohol, and which I could not obtain crystallized. The analysis of the base, of the muriate, and of the platinum salt led to the following formulæ:—

Papaverine	$C^{40}\ H^{21}\ NO^8$.
Muriate	$C^{40}\ H^{21}\ NO^8\ ClH$.
Platinum salt	$C^{40}\ H^{21}\ NO^8\ ClH,\ PtCl^2$.

This new body is consequently distinct from the bases hitherto discovered in opium; and it is well characterized by its salts and their dissimilar oily and crystalline nature, which do not allow of its being mistaken for narcotine, to which the *pure* base has otherwise some resemblance.—Liebig's *Annalen*, April 1848.

On Pyrotartaric Acid and its Salts. By A. E. Arppe.

Preparation of the Acid.—Millon and Reiset have described a very excellent method of preparing pyrotartaric acid, but which has hitherto passed unnoticed. In their paper on chemical phænomena produced by contact*, they state among other things, that racemic acid mixed with pumice-stone, or tartaric acid with platinum-black, yield on dry distillation a product which is almost colourless, and is very readily converted by evaporation into a crystalline mass, which they ascertained to be pyrotartaric acid. Led by this statement, I mixed some pulverized crystals of tartaric acid with pulverized pumice-stone in equal parts, and subjected the mixture, in a capacious retort of green glass over a charcoal fire, to dry distillation. The operation proceeds very quietly until the decomposition is complete, and a dark brown mass is left in the retort; carbonic acid, water, some acetic acid and empyreumatic oil pass over with the pyrotartaric acid, and float as a thin layer upon the distillate.

When the distillation is terminated, which supposing 2 lbs. of tartaric to have been employed occupies about twelve hours, the liquid which has passed over, and which is extremely acid, is mixed with water and the oil separated from the acid by means of a moistened filter; it is then evaporated at a gentle heat to incipient crystallization, and set aside. It soon solidifies to a highly-coloured crystalline mass, which smells of empyreumatic oil and acetic acid; and after it has been pressed between blotting-paper, has a light brown colour. This impure acid may now be purified by spreading it out between sheets of blotting-paper which have been moistened with alcohol; but

* Chem. Gaz., vol. i. p. 701.

as this would entail a considerable loss of acid, it is more advantageous to spread the impure acid upon a thick layer of filtering-paper, to surround it with small glass vessels containing alcohol, and to cover the whole with a large bell-glass. The alcoholic vapours are precipitated upon the empyreumatic oil, and dissolve this in preference; the coloured solution is imbibed by the blotting-paper, and the acid, with the loss of a small portion, is left of a perfectly white colour. However, it is still not perfectly pure, as is readily evident from its odour; it is therefore dissolved in water, digested for some time at a gentle heat with nitric acid, and evaporated to crystallization. It is generally rendered so pure by *one* such treatment, that it is merely requisite to melt it to expel the excess of nitric acid, in order to obtain a product which is perfectly colourless and free from smell. I must observe, with regard to the use of nitric acid for purifying the pyrotartaric acid, that the latter must possess a certain degree of purity before it can be treated with the nitric acid; for only the pure or nearly pure pyrotartaric acid resists the decomposing action of nitric acid, while the impure is entirely destroyed, and yields several unexamined products of decomposition. The quantity of pure pyrotartaric acid obtained according to this method amounts nearly to 7 per cent. of the tartaric acid employed; and is consequently far more considerable than that furnished by the dry distillation of tartaric acid alone or of the bitartrate of potash, which can scarcely be estimated at 1 per cent. The other advantages of this method are, that the operation goes on very quietly and safely, and that the product is much purer than when obtained by any other mode of preparation.

Properties and Composition of Pyrotartaric Acid.—A solution of pyrotartaric acid crystallizes very readily; by evaporation over sulphuric acid in dry air, it can be obtained in transparent prisms which are nearly 2 lines in length, truncated at the terminal edges, and belong to the clinorhombic system. The crystals adhere so as to form spherical or discoid groups. A pure solution of pyrotartaric acid does not effloresce; but if somewhat impure, especially if it contain nitric acid, the sides of the vessel are entirely coated on evaporation with a crystalline crust. The agreeable acid and cooling taste of pyrotartaric acid calls to mind that of tartaric and citric acid. The acid is perfectly free from smell; it melts at 212°, and begins to fume; it boils at 374°, but the thermometer gradually rises to 428°, owing to a change of the acid which will subsequently be described. After solidification it forms a white, crystalline, dull mass; it is so soluble in water that 1 part is taken up by $1\frac{1}{2}$ part water at 68°. The aqueous solution is neither decomposed by evaporation nor by boiling. Æther and alcohol also dissolve it in large quantity. Sulphuric acid blackens it on boiling; muriatic, nitric and acetic acids dissolve it unaltered. It is a much more powerful acid than carbonic acid, which it expels from its combinations with effervescence.

The composition of the acid melted at 212° was ascertained by burning it with oxide of copper and oxygen, and by the analysis of the silver salt. The samples burnt had been distilled,—I. from pure

tartaric acid, II. from cream of tartar, and III. from tartaric acid mixed with pumice-stone. I obtained in 100 parts—

	I.	II.	III.			
Carbon	45·50	45·57	45·57	5 =	375	45·43
Hydrogen..	6·09	5·93	6·02	4	50	6·06
Oxygen....	48·41	48·50	48·41	4	400	48·49

The silver salt, which left on combustion 62·40 per cent. silver, is composed according to the formula $C^5 H^3 O^3 + AgO$ (Ag = 1350), which requires 62·43 per cent. silver. The atomic weight of the anhydrous acid is according to experiment 713·1, and to calculation 712·5, and the crystallized acid must be expressed by the formula advanced by Pelouze, $C^5 H^3 O^3 + HO$.

Anhydrous Pyrotartaric Acid.—I have succeeded in obtaining crystallized pyrotartaric acid in the anhydrous state. I observed that the acid when melted or heated somewhat higher gave off a dense odour resembling that of acetic acid, which produced coughing, and that after long boiling in a glass tube it experienced a very interesting change. It could now no longer be made to crystallize, or only partially; and the portion which remained liquid had no acid reaction, and separated on the addition of water in the form of oily drops, which however gradually disappeared, while the reaction of pyrotartaric acid again made its appearance.

After these observations I attempted to prepare the anhydrous acid directly by the distillation of the crystallized acid. The oily substance always made its appearance, and collected in the receiver in large quantity; but it was rendered impure by water or by hydrated acid to such a degree that the liquid which had passed over generally solidified to a smeary crystalline mass.

Having convinced myself that it was impossible to deprive the pyrotartaric acid of its water in this manner, I mixed it with some fused phosphoric acid, and subjected the mixture to dry distillation. On the first action of heat the pyrotartaric acid loses its basic water, and a colourless oily liquid distils over; but soon the mass in the retort begins to acquire a brown colour, on which account the liquid portion must be poured into another retort, and only two-thirds of it distilled off at about 374°.

The oil which is obtained in this manner possesses the following properties;—It is perfectly colourless, has no smell at 68°, but at 104° smells of acetic acid; at first it tastes sweetish, then acrid, and finally acid like pyrotartaric acid; when swallowed, it produces a suffocating sensation in the throat; it is heavier than water, remains liquid at 14°, boils at 446°, and evaporates almost wholly without decomposition; it is quite neutral, is readily dissolved by alcohol, and again precipitated from this solution by water in oily drops. These however gradually disappear, and are converted into crystals of pyrotartaric acid. The oil experiences the same change by the action of alkalies, only that the metamorphosis is much more rapidly effected than by water.

With respect to the composition of this substance no doubt can

prevail after what has been stated respecting its mode of origin and its properties; moreover, the theoretical view of its constitution was completely confirmed by analysis; it afforded—

Carbon.....	52·65	5 =	375·0	52·63
Hydrogen	5·20	3	37·5	5·26
Oxygen	42·15	3	300·0	42·26

Pyrotartrates.—With respect to the pyrotartrates, of which the author has examined and analysed a large number, we shall merely give in this place a tabular arrangement of their formulæ.

$$C^5 H^3 O^3 = \overline{Pt}.$$

I. *Acid Salts.*

$CaO\,\overline{Pt} + 5HO\,\overline{Pt} + 2HO$	$SrO\,\overline{Pt} + HO\,\overline{Pt} + 2HO$
$Fe^2 O^3\,\overline{Pt^3} + 15HO\,\overline{Pt} + 3HO$	$KO\,\overline{Pt} + HO\,\overline{Pt}$
$GO\,\overline{Pt} + 3HO\,\overline{Pt}$	$NaO\,\overline{Pt} + HO\,\overline{Pt}$
$NiO\,\overline{Pt} + 3HO\,\overline{Pt}$	$AmO\,\overline{Pt} + HO\,\overline{Pt}$
$BaO\,\overline{Pt} + HO\,\overline{Pt} + 2HO$	$3BaO\,\overline{Pt} + 2HO\,\overline{Pt} + 3HO$

II. *Neutral Salts.*

$AgO\,\overline{Pt}$	$KO\,\overline{Pt} + HO$	$BaO\,\overline{Pt} + 2HO$	$CoO\,\overline{Pt} + 3HO$
$PbO\,\overline{Pt}$	$SrO\,\overline{Pt} + HO$	$CaO\,\overline{Pt} + 2HO$	$CoO\,\overline{Pt} + HO$
$ZnO\,\overline{Pt}$	$ZnO\,\overline{Pt} + HO$	$CoO\,\overline{Pt} + 2HO$	$MnO\,\overline{Pt} + 3HO$
$Fe^2 O^3\,\overline{Pt}$		$CuO\,\overline{Pt} + 2HO$	$MnO\,\overline{Pt} + HO$

$NiO\,\overline{Pt} + 2HO$	$MgO\,\overline{Pt} + 4HO$	$ZnO\,\overline{Pt} + 3HO$	$MgO\,\overline{Pt} + 6HO$
$PbO\,\overline{Pt} + 2HO$	$MgO\,\overline{Pt} + HO$	$ZnO\,\overline{Pt} + HO$	$NaO\,\overline{Pt} + 6HO$

III. *Basic Salts.*

$Al^2 O^3\,\overline{Pt^2} + HO$	$3PbO, \overline{Pt}$	
$Fe^2 O^3\,\overline{Pt^2} + 5HO$	$2CuO, \overline{Pt} + 2HO$	$2Bi^2 O^3, \overline{Pt^3} + 2HO$
$3Fe^2 O^3, \overline{Pt}$	$2SnO, \overline{Pt}$	$2Fe^2 O^3, \overline{Pt^3} + HO$
$9Fe^2 O^3, \overline{Pt} + HO$	$2ZnO, \overline{Pt} + HO$	$2U^2 O^3, \overline{Pt^3} + HO$

Liebig's *Annalen*, lxvi. p. 73.

On the Colouring Matter of the Morinda citrifolia.
By Thomas Anderson, Esq., M.D.

The chemistry of the colouring matters has perhaps scarcely as yet met with the extended and complete investigation which the importance of the subject, in a theoretical and practical point of view, appears to deserve. The attention of chemists has been almost exclusively directed to the study of a comparatively small number of these substances, such as indigo, logwood and the colouring matters of the lichens, which have been well and completely investigated; while the remaining, and by far the more extensive class, has received only a very partial and imperfect examination. To the latter, however, belong some of the most important of our dyes; and among

others, the most valuable and indispensable of all, madder namely, the chemistry of which forms a problem as yet very far from being solved.

But madder is only one member of an extensive class of dye-stuffs, each of which contains one or more colouring matters, the chemical constitution and relations of which are almost entirely unknown; and it may seem surprising that, with the important results obtained from those already examined before them, chemists should not have attempted to work out more completely than has yet been done the rich mine of facts which they present, and the full exploration of which is equally important to theoretical chemistry and to its practical applications. The reason however in all probability is, that they have been deterred from the investigation by the small quantity of actual colouring matters which most of these substances contain, and the tedious and complicated processes requisite for their preparation. In indigo, and those which have been fully investigated, the colouring matters are supplied to us in the arts in any quantity, and in a state approaching at least to purity; but in roots and plants the case is very different, as they there constitute only a minute fraction of the whole mass, from which their separation is always attended by difficulties, and necessitates operations on a larger scale than is either convenient or customary in a chemical laboratory. I have experienced this difficulty to a considerable extent in the investigation of the colouring matter to be treated of in the following communication, which has been somewhat restricted by the limited quantity of the substance at my disposal.

The subject of these experiments was imported into Glasgow, some time since, under the name of Sooranjee, with the intention of introducing it as a substitute for madder in the art of dyeing. For this purpose it was, on its arrival, submitted for trial to some of the most experienced and skilful calico-printers in Glasgow, all of whom concurred in declaring it not to be a dye at all, and to be totally destitute of useful applications. My friend Professor Balfour happening to hear of this circumstance, was so good as to obtain for me a quantity of the root, which has enabled me to submit it to a chemical investigation. At the time I received the substance no information could be got with regard to the plant from which it was obtained; but at the request of Dr. Balfour the importers took the trouble of writing to their correspondents in Bombay, for the purpose of obtaining specimens of the plant or its seeds. The result of this application was, that we soon received a small packet of seeds, the label of which denoted that they were those of the sooranjee or soorinjee plant, the *Morinda citrifolia* of botanists. As this plant has been long and familiarly known as yielding one of the most extensively employed native Indian dyes, and as no authority was given with the seeds for the determination of the species, it was considered desirable to substantiate it by growing them, and examining the plant itself. They were accordingly sown, both in the Botanic Garden and in the garden of Professor Syme at Milbank; unfortunately however not a single seed germinated, and we were com-

pelled to content ourselves with the less satisfactory process of determining the plant by the characters of the seed itself. By a comparison with the plates of Gærtner's work*, they are found to agree very closely with his figures of the seeds of the *Morinda citrifolia*, and certainly belong to a species of the genus. Of this genus six or seven species are known to produce dyes†; but of these two only are important, the *M. citrifolia* of Linnæus and the *M. tinctoria* of Roxburgh, both of which are extensively cultivated in various parts of India, for the sake of the dye they contain. According to Dr. Balfour, however, some confusion exists with regard to these two species, which differ so slightly that it is doubtful whether they ought not to be conjoined, the sole difference consisting in the leaves, which are shining in the *citrifolia*, and not shining in the *tinctoria*, in the former oval, in the latter oblong. All things taken into consideration, Dr. Balfour is of opinion that we are perfectly safe in referring the sooranjee to the *Morinda citrifolia*, which has been long described as the source of the native dye.

Sooranjee is the root of the plant, and is imported cut up into pieces from one to four inches in length, and varying in diameter from half down to nearly an eighth of an inch. On the small pieces the bark is thick, and forms a large proportion of the whole root, but on the larger fragments it is much thinner. Its external colour is pale grayish-brown; but when broken across, it presents colours varying from fine yellow to brownish-red, and confined principally to the bark. The wood itself has only a slight yellowish shade, deepest in the centre, and scarcely apparent close to the bark; but it is coloured dark red by alkalies, indicating the presence of a certain quantity of colouring matter in it. The bark is readily detached, and its inner surface, as well as that of the wood, has a peculiar silvery appearance, most apparent on the large pieces and almost entirely absent in the smaller. Boiled with water, it gives a wine-yellow decoction, and with alcohol a deep red tincture.

Morindine.—For the preparation of the colouring matter of sooranjee, to which I give the name of Morindine, I at first attempted the use of boiling water, in which my preliminary experiments had shown it to be pretty soluble; I found however that this method was inapplicable, as the decoction contains a quantity of mucilaginous matter, which hinders the filtration of the fluid. The use of alkalies, in which the colouring matter is rapidly dissolved, likewise proved abortive, and I had finally recourse to alcohol, which succeeded perfectly. The bark of the root, separated from the woody portions and ground to fine powder, was boiled with six times its weight of rectified spirit, and the tincture filtered boiling hot. Its colour was deep brownish-red, and on cooling it let fall the greater quantity of the colouring matter as a brown flocculent precipitate, containing the morindine, contaminated by another red colouring matter which exists in the root in small quantity only. A second

* De Fructibus et Seminibus Plantarum, vol. i. p. 144.

† In addition to those above mentioned, colouring matters are contained in *Morinda multifida*, *angustifolia*, *chachuca* and *umbellata*.

decoction, with an equal quantity of spirit, gave a paler solution, from which morindine was deposited with a much smaller quantity of the red colouring matter. This treatment was repeated over and over again, as long as the tincture deposited anything on cooling; and every successive boiling produced it purer than the preceding, until at length from the final decoctions it made its appearance in the form of minute radiated crystals of a yellow colour. By successive crystallizations from alcohol of 50 per cent., the red matter with which it was mixed was entirely removed, and the morindine obtained of a fine yellow colour. It was still however impure, and contained a quantity of ash, amounting in one experiment to 0·47, in another to 0·32 per cent. The separation of this could not be effected by crystallizations from alcohol alone; but after some trouble I succeeded in removing it completely by solution in alcohol slightly acidulated by hydrochloric acid, from which it crystallized in a state of purity.

Morindine is deposited from alcohol in minute needles, which if the solution be dilute make their appearance in radiated circles attached to the glass, and resembling in their arrangement the crystals of wavellite. They are extremely soft, and on being detached, collected on a filter and dried, mat together into a mass, presenting a rich sulphur-yellow colour and satiny lustre. These crystals are sparingly soluble in cold alcohol, much more so in boiling spirit, especially if dilute; and the fluid on cooling is filled with a mass of bulky needles, which when dried shrink into a very small bulk. They are much less soluble in absolute alcohol, and totally insoluble in æther. Water dissolves morindine in the cold very slightly, although sufficiently to communicate a yellow colour to the fluid; at the boiling temperature however it is readily taken up, and again deposited on cooling as a gelatinous mass, destitute of all traces of crystallization, which stops up the pores of the filter, and prevents the separation of the mother-liquor. It dissolves in solutions of the alkalies with a fine orange-red colour. With concentrated sulphuric acid it gives a deep purple, which is violet in thin layers. After twenty-four hours' contact the solution on being diluted deposited yellow flocks of the colouring matter in an altered condition, as it was now totally insoluble in cold water, and gave with ammonia a violet and not an orange solution. Nitric acid, spec. grav. 1·38, dissolves morindine slowly in the cold with a deep brownish-red colour. The application of heat immediately produces violent action, the brown colour disappears, and nitrous acid fumes are evolved. The fluid, after long-continued boiling with the acid and neutralization with ammonia, gave no precipitate with salts of lime.

Solution of morindine gives with subacetate of lead a precipitate depositing itself in crimson flocks, which is extremely unstable, and cannot be washed without losing colouring matter. With solutions of baryta, strontia and lime, it gives bulky red precipitates, sparingly soluble in water. Perchloride of iron produces a dark brown colour, but no precipitate. When its ammoniacal solution is added to that of alum, the alumina precipitated carries down with it the morindine

as a reddish lake; and when added to perchloride of iron, a brown precipitate is thrown down, which cannot be distinguished from pure peroxide of iron, but which contains morindine, as the supernatant fluid is colourless.

Heated in close vessels, morindine melts into a deep brown fluid, and boils at a high temperature, with the evolution of an exceedingly beautiful orange vapour resembling that of nitrous acid, which deposits itself on cold substances in fine red needles of considerable length. A bulky charcoal remains in the vessel.

The analyses of morindine were performed with oxide of copper, and upon substance which had been carefully dried for a long time at 212°. The results were as follows:—

	I.	II.	III.	Equivs.	Calculation.	
Carbon	55·46	55·40	55·39	28	=2100·0	55·44
Hydrogen	5·19	5·03	..	15	187·5	4·95
Oxygen	39·35	39·57	..	15	1500·0	39·61
	100·00	100·00			3787·5	100·00

The formula thus ascertained brings out an interesting relation between morindine and the colouring matters of madder, and more especially that one which is obtained by the sublimation of madder-purple. From his analysis of this substance, Schiel* deduces the formula $C^7 H^4 O^1$. As this however is no more than the simplest expression of the analytical results, and as all the other madder colouring matters examined contain 28 equivs. of carbon, we are justified in supposing its real constitution to be represented by quadruple of that formula, or $H^{28} H^{16} O^{16}$, which differs from that of morindine by a single equivalent of water only. The unsublimed madder-purple is also connected, though more remotely, with morindine, and differs only by containing 5 equivs. of hydrogen less, its formula according to Schiel being $C^{28} H^{10} O^{15}$.

Moreover this similarity is not confined to their formulæ only, but extends itself over all their physical and chemical properties, which approximate very closely, although they are sufficiently distinct to preclude the possibility of their being confounded with one another. And this is a point well-worthy of observation, as illustrating the similarity in chemical constitution of plants so nearly related in the botanical system; the *Morinda* belonging to the natural family *Cinchonaceæ*, which by many botanists is considered as merely a section of the *Rubiaceæ*, of which madder is the type.

This similarity however does not extend itself to their properties, as dyes, in which respect they differ in a very remarkable manner. I have already mentioned that the calico-printers had entirely failed in producing a colour by means of sooranjee; and this I have fully confirmed as regards the common mordants. I digested morindine for a long time, in a gradually increasing heat, with small pieces of cloth mordanted with alumina and iron; but nothing attached itself,

* Chem. Gaz., vol. v. p. 77.

and the mordants, after boiling for a minute or two with soap, were found to be unchanged. Even with the root itself alum mordant only acquired a slight reddish-gray shade, and iron became scarcely appreciably darker in colour. The case was different however when cloth mordanted for Turkey-red was employed. I obtained from Glasgow pieces of calico prepared for Turkey-red both by the old and new processes; and I found that both acquired with morindine, in the course of a couple of hours, or even less, a dark brownish-red colour, devoid of beauty, but perfectly fixed. These observations agree with the account given by Mr. Hunter of the method of dyeing with the *M. citrifolia* employed by the Hindoos. The cloth is first soaked in an imperfect soap made by mixing the oil of the *Sesamum orientale* with soda-ley. After rinsing and drying, it is treated with an infusion of myrobalans (the astringent fruit of the *Terminalia chebula*), and exposed for four or five days in the sun. It is then steeped in solution of alum, squeezed, and again exposed for four or five days. On the other hand, the powdered roots of the *Morinda* are well-rubbed with oil of sesamum, and mixed with the flowers of the *Lythrum fruticosum* (Roxburgh) or a corresponding quantity of *purwas* (the nut-gall of a species of *Mimosa*). The whole is introduced along with the cotton into a large quantity of water, and kept over a gentle fire for three hours, when the temperature is brought to the boiling-point. The red colour so obtained is, according to Mr. Hunter, more prized for its durability than its beauty. This is simply a rude process of Turkey-red dyeing. He also mentions that, by means of iron mordant, a lasting purple or chocolate is obtained; but in this case the colour is probably affected by the tannine of the astringent matters employed in the process.

Morindone.—It has been already mentioned, that morindine when heated is entirely altered, a quantity of carbonaceous matter being left, and a crystallizable principle sublimed, differing in its properties from the original substance. To it I give the name of Morindone.

Morindone is obtained by sublimation in the form of long needles, which under the microscope are found to be four-sided prisms, terminated by a single oblique face, and of an exceedingly rich and beautiful red colour. They are totally insoluble in water both hot and cold, but dissolve readily in alcohol and æther, and the solutions by slow evaporation deposit crystals. The alkalies dissolve it with a magnificent violet colour. In strong sulphuric acid it is also soluble, with the same intense violet colour, and it is precipitated on diluting the acid. Its ammoniacal solution gives a fine red lake when added to solution of alum, and a cobalt-blue precipitate with baryta-water. The quantity of morindone which I was able to obtain for analysis was too small to admit of accurate results, or of all the precautions for its purification which would have been resorted to had I possessed a larger quantity. The sublimed crystals were simply washed with æther, in order to remove empyreumatic matters, and then dried at 212°. Analysis gave the following results:—

	Experiment.	Equivs.		Calculation.
Carbon.....	65·81	28	= 2100·0	65·11
Hydrogen	4·18	10	125·0	3·87
Oxygen	30·01	10	1000·0	31·02
	100·00		3225·0	100·00

Of course it is impossible to consider a formula as established by a single analysis upon so small a quantity. I think it probable however that that given above may be the true one, and that the excess of carbon was due to imperfect separation of empyreumatic matters, as, to avoid loss by solution, I washed with the smallest possible quantity of æther. That morindone is formed from morindine by the elimination of water derives confirmation from the change which the latter substance undergoes in contact with sulphuric acid. As already mentioned, it then becomes insoluble in water, and gives a violet colour with alkalies similar to that produced by morindone; and as sulphuric acid in general acts by removing water, the probability is that it has deprived the morindine of 5 equivs., and converted it into morindone; at the same time this is a point which can only be determined by analysis, and the quantity which I obtained was not nearly sufficient for that purpose. Should further experiments establish $C^{28}\,H^{10}\,O^{10}$ as the true formula of morindone, we have another simple relation with the madder colouring matters, as it would differ from madder-red by a single equivalent of water, the formula for that substance, according to the analysis of Schiel, being $C^{28}\,H^{9}\,O^{9}$. It would also be polymeric with gentianine, for which Baumert* has established the formula $C^{14}\,H^{5}\,O^{5}$.

Morindone is a true colouring matter, and is capable of attaching itself to common mordants. It gives with alumina a deep rose-red, and with iron violet and black; but the colours are not very stable, and it has a strong tendency to attach itself to the unmordanted parts of the cloth and to degrade the white. Morindine, after treatment with sulphuric acid, is capable of attaching itself to ordinary mordants.

The discovery of a peculiar colouring matter capable of fixing itself exclusively on Turkey-red mordant, is of interest as establishing the existence of a peculiar class of dyes hitherto totally unsuspected, a class which may be extensive, and may yield important substances. It may serve also in some respects to clear up the *rationale* of the process of Turkey-red dyeing, which has long been a sort of opprobrium of chemistry. Although that process has been practised for a century in Europe, and has undergone a variety of improvements, no clear explanation of it was for a long time given; but it was supposed that, by the action of the dung, of which large quantities are employed, the cloth underwent a species of *animalisation*, as it was called, by which it acquired the property of receiving a finer and more brilliant colour than could be attached to it by purely mineral mordants. Recent experiments have however shown that the oil,

* Chem. Gaz., vol. v. p. 446.

which is largely employed in the process, undergoes decomposition by long exposure to the air in contact with decomposing animal matter, and is converted into a sort of resinous matter, which constitutes the real mordant for Turkey-red. This has been pretty clearly made out by the experiments of Weissgerber*. He found that when cloth had been treated with oil, so as to give when dyed a fine rose-red colour, he could, by digestion with acetone, extract from it the altered oil; and as it was removed the cloth gradually lost the power of attracting the colouring matter of madder, until, when it was entirely separated, the cloth passed through the dye without acquiring any colour. On the other hand, he found that, by applying the substance extracted by acetone in sufficient quantity to cloth, he could obtain the richest and deepest colours with madder, without the addition of any other substance whatsoever. These observations receive additional confirmation from the experiments detailed in the present paper, as it must be sufficiently obvious that the dark red colour obtained on Turkey-red mordant with morindine, must be entirely irrespective of the alumina, on which that substance is incapable of fixing.

I fully agree with the opinion expressed by Persoz, that the use of alum mordant, which is at present always employed in Turkey-red dyeing, will be entirely abandoned so soon as calico-printers have learned the method of modifying at will the oil which they employ, so as to bring it at once into the state in which it acts as a mordant. Some steps have been made in this direction by making use of some chemical agents, as nitric acid and chloride of lime, for the purpose of acting on the oil; but the improvements which have been effected stop far short of what I believe will eventually be effected when the system of pure empiricism which has been all along employed in this particular process of dyeing is abandoned, and the subject submitted to really scientific investigation. It is understood that M. Chevreul has entered upon the inquiry, and in his hands there is little doubt but that it will meet with a satisfactory solution.—From the *Transactions of the Royal Society of Edinburgh.*

On the Crystalline Hydrate of Sulphurous Acid. By M. Döpping.

When pure sulphurous acid is passed into water, the receiver being kept cool by the external application of ice, the hydrate of sulphurous acid separates in crystals as soon as the water is saturated with the gas. These crystals re-dissolve a few degrees above the melting-point of ice, and again separate on subsequent cooling a few degrees below 32°. They then form a crystalline mass consisting of cubes.

These crystals have the composition SO^2, HO; they may be separated from the supernatant liquid at 26° F., dried between blotting-

* Persoz, sur l'Impression des Tissus, vol. iii. p. 176.

paper, and preserved in dry bottles; between 30° and 27°, they begin to become moist, and then melt with evolution of sulphurous acid. If placed over sulphuric acid at 23°, the sulphurous acid compound is gradually deprived of water and decomposed.

For analysis the author separated the crystals upon a funnel, and then pressed them between blotting-paper; they were weighed in sealed tubes at 32°, and then mixed with strong chlorine-water, when the sulphurous acid was determined as sulphuric acid. Analysis furnished—

Sulphurous acid.....	76·02	79·16	76·82	1=32	78·05
Water.....	23·98	20·84	23·18	1 9	21·95

These cubic crystals are consequently different from the compound which is obtained, according to De la Rive, in laminæ by cooling moist sulphurous acid gas, and in the form of snow, on the evaporation of the liquid acid, since De la Rive found it to contain approximatively 80 per cent. of water. According to Döpping, another compound of sulphurous acid with water appears to exist. If, for instance, the liquid from which the hydrate above-described has separated is exposed to a temperature of 21°–19°, it solidifies to a mass of laminar crystals; as the temperature approaches 32°, the crystals again become liquid, and at 28° they had all disappeared, in which respect these crystals differ from those above described. Döpping states that he was not able to obtain De la Rive's compound.—*Bull. de St. Pétersb.*, vii. p. 100.

On Mellitic Acid and the Products of its Metamorphosis.
By Dr. H. Schwartz.

Having been furnished with a considerable quantity of pure honey-stone, I was induced to enter upon an examination of some points which had been left in a state of uncertainty, with respect to the relations existing between mellitic acid and the products of its metamorphosis.

Ammonia Salt.—The ammonia salt was easily prepared according to the method described by Wöhler, and the greater portion was obtained perfectly colourless and pure by repeated crystallization. As the amount of water in the ammonia salt had never been determined*, I submitted to analysis some beautiful, large, perfectly transparent crystals, dried over chloride of calcium. The combustion was made with a platinum tray, and towards the end of the operation a current of oxygen was employed; before the coarsely-pounded oxide of copper a closely-wound roll of sheet copper was inserted, the surface of which had been previously reduced in a cur-

* As the author makes no allusion to Prof. Marchand's paper on this subject, which appeared in this Journal for May 15, p. 189, it is probable his paper was sent to press about the same time. Dr. Schwartz's paper is contained in the *April* number of Liebig's 'Annalen,' which however was not published before the 24th of *June*.—Ed. *Chem. Gaz.*

rent of hydrogen. I obtained 23·906 per cent. carbon and 7·162 hydrogen, and on analysis with soda lime, 13·612 nitrogen, quantities which correspond to the formula $NH^4O, C^4O^3 + 3HO$.

Crystallized Mellitic Acid.—To obtain the free acid, the silver salt was prepared from the pure ammonia salt, and after complete washing decomposed with dilute muriatic acid. It is very difficult to obtain the silver salt, and consequently the acid, free from ammonia, and succeeds only by adding the solution of the ammonia salt in drops to an *excess* of a boiling solution of nitrate of silver. The salt prepared without this precaution acquires a violet-brown colour when heated, while the pure salt remains perfectly white at 392°.

The pure crystallized acid lost, after being dried *in vacuo*, mere traces of moisture at 392°. Two analyses confirmed the composition formerly advanced, and afforded—

			Calculated according to the formula $HO + C^4O^3$.
Carbon....	42·122	42·173	42·146
Hydrogen..	1·830	1·706	1·750
Oxygen ..	56·048	56·121	56·104

This composition was likewise confirmed by the repeated analysis of the silver salt, which led to the formula AgO, C^4O^3 for the salt dried at 212°. The lead salt, dried at 212°, is represented by the same formula. In preparing this salt, the same precaution is necessary as with the silver salt.

Baryta Salt.—This is obtained by double decomposition as a thick gelatinous mass, which however shrinks into shining crystalline scales. From very dilute solutions it is obtained in delicate needles. After drying it forms a silvery laminar mass; on combustion, even in a current of oxygen, it requires a long time to burn the last trace of carbon. Heated up to 212°, it merely loses hygroscopic water, but retains 1 atom of combined water, which curiously enough is only expelled at 626°. According to theory this atom requires 6·742 per cent.; the author obtained in three analyses 6·659, 6·372 and 6·658 per cent. The salt, heated up to 626°, furnished 19·226 and 19·289 carbon, and 60·813–60·783 baryta; theory requires 19·314 per cent. carbon and 61·403 baryta. In some analyses it was rendered evident that the salt at times contained a mixture of an acid salt, which increased the amount of carbon, decreased that of the baryta, and moreover furnished water on combustion.

The Copper Salt is, as is well known, crystalline, and can even be obtained in blue crystals capable of measurement; they contain 4 atoms of water, of which 3 are expelled at 212°, the salt turning green; at a higher temperature the fourth atom begins to be given off, but it is not entirely expelled even at 446°.

Mellitic Æther appears not to exist, according to the numerous unsuccessful experiments made by both Prof. Wöhler and myself. It could not be produced by distilling mellitic acid with alcohol and sulphuric acid, nor by passing muriatic or sulphurous acid gas into

alcohol mixed with mellitic acid, nor by distilling the ammoniacal salt with sulphovinate of lime. It was equally impossible to obtain a combination with methylic oxide, and similar experiments to obtain euchronic æther were equally without success. It may be stated that all experiments to produce mellitic acid from succinic acid, or the fatty acids by means of the most different oxidizing agents, proved unsuccessful.

Euchronic Acid.—To prepare this acid, it is best to heat the mellitate of ammonia in a broad, shallow porcelain dish, over a charcoal fire, constantly stirring to prevent it from aggregating until no more ammonia is evolved, and the salt is converted into a pale yellow powder. The amount of euchronic acid obtained is far greater, and that of paramide far less, if the mass, instead of being exhausted with cold water, is digested with a little water between 86° and 104°, and the solution filtered immediately into tolerably strong muriatic acid; the residue of paramide is removed from the filter, and again treated in the same manner with a little water, and this is repeated as long as the liquid dropping into the muriatic acid deposits crystals of euchronic acid. This is collected on a filter, washed two or three times with cold water, pressed, and purified by frequent crystallization from dilute nitric or muriatic acid, which at the same time removes a trace of ammonia that most tenaciously adheres to it. The mother-leys, which still contain some euchronic acid besides chloride of ammonium, are evaporated to dryness, the mass dissolved in caustic ammonia, heated to boiling to convert the euchronic into mellitic acid, and this precipitated by a salt of baryta, or after removal of all the free ammonia by a salt of copper. The analyses of the pure acid, dried at 392°, furnished the following results:—

				Calculated according to $2HO+C^{12}NO^6$.
Carbon	47·309	47·554	47·389	47·408
Hydrogen	1·423	1·505	1·558	1·312
Nitrogen	9·263	9·101	..	9·207
Oxygen.....	42·005	41·840	..	42·073

The crystallized acid moreover contains 2 atoms or 10·579 per cent. of water. As Wöhler has shown, euchronic acid may be considered as a conjugate mellitic acid consisting of 2 atoms of mellitic acid and 1 of a body of the composition $C^4N = (2C^4O^3 + C^4N)$.

The above composition was fully confirmed by the analysis of the silver salt dried at 392°, although it was not easy to obtain it free from an admixture of an acid salt, which increased the amount of carbon, decreased that of the silver, and moreover yielded water on combustion. In general a remarkable difficulty was met with in obtaining the euchronates of a certain degree of saturation unmixed and free from mellitates. This was especially the case with the baryta salt. By the gradual addition of barytic water to a hot solution of euchronic acid in excess, a pale yellow powder was obtained, which furnished on analysis 51·4 per cent. baryta, 25·8 carbon, and

0·5 hydrogen, which agrees closely with $BaO, HO + C^{12}NO^6$. A yellow lead salt has an analogous composition.

Paramide.—After what has been stated above, that the amount of euchronic acid can be very considerably increased and that of paramide diminished, if the mass left after heating the mellitate of ammonia is digested repeatedly with water at a temperature between 86° and 104°, it appears certain that the residue either contains a bieuchronate of ammonia, which only dissolves after long contact with hot water, or that the paramide, if the heat has not been too high in its production, is converted, by long contact with water of the above temperature, into euchronate of ammonia. The more paramide is obtained, the higher the temperature at which the ammonia salt is decomposed. That it is not produced from the euchronate by too high a temperature was already known, from the fact that the pure salt may be heated without alteration up to 392°.

I have confirmed the earlier statements respecting the composition of paramide, which had been partially deduced from its mode of production and metamorphoses, by several analyses:—

			Calculated according to C^8NHO^4.
Carbon	50·006	50·199	50·565
Hydrogen..	1·525	1·539	1·050
Nitrogen ..	13·468	..	14·729
Oxygen....	35·001	..	33·656

The differences between the found and calculated numbers may be ascribed to the retention of a small quantity of euchronate of ammonia or an admixture of the following substance. With the behaviour of paramide towards water and alkalies at a high temperature we are already acquainted. According to a recent experiment of Wöhler, when it is boiled with a solution of acetate of lead, it is converted, with production of acetate of ammonia, into pure mellitate of lead.

When caustic ammonia is poured over it, it immediately turns yellow, swells to a voluminous mass, and partially dissolves. If this solution is immediately added to muriatic acid, a snowy-white powder falls, which is seen under the microscope to consist of delicate acicular crystals. It is somewhat soluble in hot water, but separates again as a powder on cooling. With zinc it gives the blue reaction of euchronic acid. It is dissolved by ammonia, and again precipitated by muriatic acid; but if the solution is heated or set quietly aside for a day, it is found to contain only mellitate of ammonia. After desiccation *in vacuo*, this substance lost, when heated to 338°, 3·286, 2·890, 2·916 per cent. water. The analysis of the substance, dried at 354°, gave the following numbers:—

Carbon	47·150	47·346
Hydrogen	2·041	2·166
Nitrogen.....	13·784	

Taking into consideration the circumstance that this substance is

converted by water and alkalies into mellitic acid and ammonia, the formula $C^{24} H^5 N^3 O^{14}$ is the most probable; this yields in 100 parts—

Carbon	47·563
Hydrogen	1·647
Nitrogen	13·855
Oxygen	36·935

The quantity of water which might be separated would amount to 1 atom or 2·882 per cent.

This substance, which might be called *paramidic acid*, may be formed by 3 atoms of paramide combining with the elements of 2 atoms of water, or 2 atoms of euchronic acid uniting with the elements of 1 atom of ammonia and 2 atoms of water.

Euchrone.—Wöhler has given this name to the remarkable dark blue substance which is formed by the action of zinc upon euchronic acid, and of which he assumes that it is a similar compound to colourless indigo, and the colourless or green hydroquinone produced by the assimilation of hydrogen. Notwithstanding numerous experiments, I have unfortunately not succeeded in determining positively the true nature and composition of this substance. The great instability of euchrone and the difficulty of preparing it in sufficient quantity could not be overcome. I shall pass over these experiments, and merely mention that I could not succeed in preparing it by the action of sulphuretted hydrogen, sulphurous acid, dithionites and arsenites, alloxantine, hydroquinone, oil of bitter almonds, &c., upon euchronic acid. I can only add to the two known methods of producing it by zinc and the hydrated protoxide of iron, that by a galvanic current; but it is equally obtained in insufficient quantity and unstable. When a galvanic current is passed through a solution of euchronic acid, the platinum forming the hydrogen pole becomes coated with deep blue euchrone, but which, probably because it is not a conductor, soon ceases to increase in quantity.—Liebig's *Annalen*, lxvi. p. 46.

Experiments on the Preparation of Salts of the Sesquioxide of Manganese. By R. Hermann.

The residue left on exposing the protonitrate of manganese, obtained by precipitating a solution of the sulphate with nitrate of baryta, to a faint red heat, is, according to Berzelius, the sesquioxide of manganese. The author prepared this oxide, washed it with water containing acetic acid to remove all baryta, and dried it. It lost on ignition more oxygen than corresponds to the sesquioxide, and less than the peroxide. Pure sesquioxide, free from peroxide, was obtained as a brownish-black powder by exposing small quantities of this product to a dull red heat. Thus prepared, it lost on ignition 3·50 per cent., while pure sesquioxide should lose 3·36 per cent. according to theory.

In its behaviour towards acids this sesquioxide exhibited all the properties that are known of it. With most of the mineral acids no salts could be obtained, owing to the readiness with which they are decomposed by heat. It is insoluble in cold concentrated sulphuric acid, and equally so in cold and boiling phosphoric acid. L. Gmelin has described a compound which he regards as the metaphosphate of the sesquioxide of manganese. The author endeavoured to prepare this compound, and with this view evaporated a mixture of the sesquioxide and phosphoric acid to dryness, and heated it nearly to redness. A violet mass was obtained, which partially dissolved in water with a purplish-red colour; another portion was left behind as a peach-blossom coloured powder. After long standing, light brown crystalline granules separated from the solution; they were however mixed with a second blackish substance, probably the hydrate of the peroxide of manganese; the analysis consequently did not afford compatible results; there were found 37·35, 24·83, 35·12 per cent. sesquioxide of manganese, and 48·99, 49·43, 49·91 per cent. phosphoric acid. The peach-blossom coloured powder was found to be insoluble in acids, excepting muriatic acid; even concentrated sulphuric acid decomposes but mere traces of it after long boiling. Caustic potash immediately separates oxide of manganese on the application of heat. When this compound is exposed to an intense red heat, it melts to a violet glass. On ignition in a covered crucible the salt lost 6·10 per cent.; but it had become converted into a protosalt, so that 2 atoms phosphoric acid must have combined with 2 atoms of protoxide of manganese, while the third combined with 1 atom of water; consequently only 1 atom of oxygen and 1 of water should be expelled. This loss amounts to 5·46 per cent., while the experiment gave 6·10. The results of the analysis compared with theory are as follows:—

Mn^2O^3	25·29	25·53	25·57	25·37	1	=25·43
PO^5	..	..	68·25	69·01	3	68·78
HO	..	..	6·21	5·62	2	5·79

To ascertain whether any salts of the sesquioxide of manganese could be obtained with organic acids, some protosulphate of manganese and chloride of ammonium were dissolved in water, and caustic ammonia added. A current of air was passed through the liquid, to cause the hydrated sesquioxide to separate quickly. The precipitate was first washed with water containing acetic acid, and then with pure water. This hydrate appears to part with its water at 212°. After being dried by exposure to the sun, it lost on ignition 6·14 per cent. water; the formula Mn^2O^3, which is generally admitted for this hydrate, requires 10·21, and the formula $2(Mn^2O^3) + HO$ only 5·38; no other oxide was mixed with it.

This hydrate dissolves readily in a concentrated solution of tartaric acid, forming a reddish liquid, which is easily filtered. In twenty-four hours the liquid becomes perfectly colourless, while a faintly reddish-brown coloured salt separates in minute crystals,

which are perfectly insoluble in water. At 212° it was converted into a white powder. The following analysis shows that this salt is essentially a tartrate of the protoxide of manganese :—

Carbon.....	23·36	23·36	4 =	23·63
Hydrogen	2·18	2·15	2	1·97
Oxygen	39·96	39·90	5	39·39
Protoxide of manganese....	34·50	34·59	1	35·01

The reduction of the sesquioxide to protoxide is effected at the expense of the tartaric acid, which is converted into formic acid (which may be detected in the liquid) and carbonic acid, for the gas which was disengaged was entirely absorbed by potash. Oxalic and malic acids likewise reduce the sesquioxide of manganese to the state of protoxide, a protosalt being formed and carbonic acid disengaged. The volatile acids, the formic and acetic, do not act upon the sesquioxide of manganese, nor could any combinations be obtained with benzoic and hippuric acids.—Poggendorff's *Annalen* for June 1848.

On some Pyrophosphates. By T. Fleitmann *and* W. Henneberg.

When an excess of recently-precipitated pyrophosphate of copper is boiled with a solution of pyrophosphate of soda, white crystalline crusts, insoluble in water, separate from the hot filtered liquid on cooling. On separating the liquid and concentrating it in the water-bath, a faint blue sediment separates, which is distinctly crystalline, especially on slow evaporation. It is equally insoluble in water. If the mother-ley separated from this second salt is left to spontaneous evaporation for some time, pyrophosphate of soda crystallizes from it; and finally, when the solution has acquired the consistence of a syrup, a third double salt of copper separates in groups of blue warty crystals. As the following analyses show, the second and third salts are identical with those described and analysed by Persoz. The second is the salt

$$2NaO, PO^5 + 2CuO, PO^5 + 12HO,$$

and the third

$$3(2NaO, PO^5) + 2CuO, PO^5 + 24HO.$$

The first salt is a new compound belonging to this series. All three salts melt at a red heat. They were analysed by precipitating the copper with sulphuretted hydrogen from the muriatic solution, and determining the phosphoric acid in the boiled filtered liquid by a salt of magnesia. After driving off the chloride of ammonium, the excess of magnesia was removed by baryta, or by ignition with peroxide of mercury if it existed in a state of chloride, and the soda estimated as chloride of sodium.

I. *The Double Salt*, $3(2CuO, PO^5) + 2NaO, PO^5 + 7HO$ (dried at 212°), is the first of the three salts above mentioned; the amount of water of crystallization was not ascertained, as the salt effloresces very readily. Dried at 212° it afforded—

CuO	36·36	6	36·58
NaO	9·98	2	9·52
PO^5	..	4	44·23
HO	9·59	7	9·67

II. *The Double Salt,* $3(NaO, CuO, PO^5)+2HO$ (dried at 212°), and $NaO, CuO + PO^5$ (ignited).—The results of the analyses lead to the above formulæ, which agree with those advanced by Persoz, with the exception of the amount of water:—

	Hydrated salt.	Anhydrous salt.
CuO	26·70	27·82
NaO	20·85	21·73
PO^5	48·42	50·45
HO	4·03	

III. *The Double Salt,* $2CuO, PO^5+3(2NaO, PO^5)+4HO$ (dried at 212°), and $2CuO, PO^5 + 3(2NaO, PO^5)$, ignited.—Persoz found in the hydrated state 24 atoms of water to the above proportion of pyrophosphate of copper and soda; the authors obtained in the analysis of the salt dried at 212°, 5·86 per cent. water (the formula given above requires 6·10), and of the ignited salt—

CuO	14·27	2 =	14·34
NaO	33·66	6	33·61
PO^5	52·16	4	52·05

When hydrated oxide of copper is digested with a solution of bipyrophosphate of soda, a blue solution is obtained in the cold, while a portion of the hydrated oxide is converted into a white powder. This, when prepared with a large excess of the soda salt, contains 9·5 per cent. of water after desiccation at 212°, and 41·85 per cent. oxide of copper in the fused state. These numbers agree with the composition of the salt described under I.; it would consequently appear that the following decomposition takes place:—

$$8(NaO, HO\ PO^5) + 8CuO = 3(2CuO, PO^5) + 2NaO, PO^5,$$
$$\text{and } 3(2NaO, PO^5) + 2CuO, PO^5.$$

The authors have likewise prepared the double pyrophosphate of soda and peroxide of iron described by Persoz. Pyrophosphate of iron was boiled with pyrophosphate of soda, but not in sufficient quantity to dissolve the whole, and the salt precipitated from the solution by the addition of alcohol. Persoz obtained it only in a state of solution. The authors obtained the following results for the salt dried at 212°, leading to the same formula as that assigned to it by Pelouze as regards the fixed constituents, viz.

$$2Fe^2\,O^3, 3PO^5 + 2(2NaO, PO^5) + 7HO.$$

Peroxide of iron	22·42	2 =	22·63
Soda	..	4	17·54
Pyrophosphoric acid	51·12	5	50·92
Water	9·19	7	8·91

Liebig's *Annalen,* lxv. p. 387.

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On the Combinations of Phosphoric and Arsenic Acids with Oxide of Uranium, Analysis of Uranite and Chalcolite, with a Method of determining Arsenic. *By* G. WERTHER.

PHOSPHORIC acid enters into two combinations with oxide of uranium, and probably into a third. Of the two first, one contains 1, the other 2 atoms of base to 1 atom of acid; the third probably contains 3 atoms of base to the same quantity of acid.

I. *Phosphate of the Oxide of Uranium,* $U^2O^3 + PO^5 + 5HO$, or rather $(U^2O^3 + 2HO) + PO^5 + 3HO$.—When oxide of uranium is moistened with hydrated phosphoric acid, a yellow saline mass is formed, of which one portion dissolves in boiling water, while the other remains undissolved. The solution deposits, when dried over sulphuric acid, a lemon-coloured salt in groups of distinct crystals, which are not measurable. At a gentle heat they lose a portion of their water, and become pale yellow. The remainder of the water is expelled at a red heat, and likewise almost wholly when dried for a considerable time between 338° and 392°, the salt puffing up. The salt cannot be fused, and does not part with any acid. When treated with water it is decomposed, phosphoric acid and oxide of uranium dissolving, leaving behind an insoluble basic salt. When dissolved in phosphoric acid, and ammonia is added, a yellow salt is precipitated, which contains ammonia.

The analysis of the phosphate of the oxide of uranium is accompanied with considerable difficulty; the salt is not decomposed by boiling with concentrated solution of potash, by fusion with alkalies or hydrate of baryta, or when heated with carbonate of lead. The method of combining the phosphoric acid with lead is not satisfactory, as the nitric acid requisite to dissolve the salt decomposes a portion of the phosphate of lead. On fusion with carbonate of soda, if there happens to be the least excess, a portion of the oxide of uranium is readily dissolved. After various experiments, the following mode of analysis was adopted:—The double tartrate of potash and soda was carbonized in a platinum crucible, the phosphate of uranium dropped upon it, and the mass kept at a red heat. When care is taken that none of the salt touches the platinum crucible, and the temperature is not raised higher than a red heat, there is no danger of the crucible being destroyed and phosphorus escaping.

As soon as the black mass is perfectly fused, the whole of the oxide of uranium is reduced to protoxide, and the heating is discontinued; the mass is then exhausted with water, which removes the phosphate and the carbonate of soda, leaving protoxide of uranium and charcoal on the filter. The phosphoric acid was then determined as the ammonio-phosphate of magnesia, while the protoxide of uranium was dissolved in nitric acid and precipitated with ammonia.

Instead of the reduction with carbonized tartrates, the employment of hydrogen afforded satisfactory results. The salt was heated in a current of hydrogen until it became green, and then fused with carbonate of soda or potash; as only a portion of the oxide is reduced to protoxide, sometimes a small quantity of uranium is subsequently dissolved with the alkaline salt. The following are the results obtained by these methods:—

Phosphoric acid*	26·7	..	27·49	1	27·47
Oxide of uranium	55·9	54·6	..	1	55·20
Water ..... 17·9	16·8	17·2	..	5	17·33

II. *Phosphate of the Oxide of Uranium*, $2U^2O^3 + PO^5 + xHO$. —The insoluble residue which remains in the preparation of the preceding salt contains the one now under consideration, which may also be procured in different ways. It is obtained when the acetate of the oxide of uranium is precipitated with phosphoric acid, or the nitrate with $2NaO + PO^5, HO$; but the salts prepared according to these different methods do *not* contain the same amount of water; they are all of a pale yellow colour, and generally crystalline, at least under the microscope; they are insoluble in water and acetic acid, and soluble in mineral acids and carbonate of ammonia.

$(U^2O^3 + HO) + PO^5 + 3HO$, obtained by treating oxide of uranium with dilute phosphoric acid and exhaustion with water, is amorphous, assumes a dark yellow colour at a red heat, and its original pale yellow colour on cooling. It loses 7·03 per cent. water between 248° and 338°; the remaining 1 equiv. is expelled only at a red heat. In this state it is $2U^2O^3 + PO^5$, and absorbs water when moistened. When now dried over sulphuric acid, it yielded 6·86 per cent. water; 3 equivs. water correspond to 7·01 per cent., which amount was given off on again heating the salt to 347°. The following are the results of the analysis:—

Phosphoric acid ..... 17·96	..	..	1	18·11
Oxide of uranium..... ..	72·160	..	2	72·77
Water	9·665	9·658	4	9·12

$(2U^2O^3 + HO) + PO^5 + 8HO$, air-dried, and $(2U^2O^3 + HO) + PO^5 + 6HO$ (dried at 140°), is obtained on the addition of phosphoric acid to the acetate of the oxide of uranium until no further precipitate is formed; it is a distinctly crystalline powder, of a somewhat darker yellow than the preceding, and exhibits the same behaviour when heated to redness. It afforded on analysis—

* P = 392·3; U = 746·36; H = 12·5.

	Air-dried.			Dried at 140°.			
Phosphoric acid	..	1	=16·26	..	..	1	=16·94
Oxide of uranium ..	64·78	2	65·30	67·93	..	2	68·10
Water	18·46	9	18·44	15·20	15·74	7	14·96

By the decomposition of $(2NaO + HO) + PO^5$, with the nitrate of the oxide of uranium, $U^2O^3 + NO^5$, a salt is obtained which exactly resembles the preceding one dried at 140°, and possesses the same composition. When heated to 248° it loses 6 atoms of water, but the 7th only at a red heat. The same salt was likewise formed in the liquid separated from a precipitate produced by the imperfect precipitation of nitrate of uranium with the tribasic phosphate of soda, $NaO^3\,PO^5$, on the addition of an excess of the nitrate of uranium; it formed an indistinctly crystalline pale yellow powder.

III. *Phosphate of the Oxide of Uranium*, $3U^2O^3 + PO^5$, appears to exist in some double salts. When, for instance, the nitrate is precipitated with an excess of $3NaO + PO^5$, a dark yellow salt is formed, which cakes together, and dissolves in an excess of $3NaO + PO^5$. If this be prevented, the precipitate forms a dark yellow powder, which cakes together, and like the other phosphates of uranium is insoluble in water. Acetic acid decomposes the salt, colours it yellow, and removes oxide of uranium and soda. According to the author, this salt is probably a combination of oxide of uranium and soda with phosphate of soda, $(NaO, 2U^2O^3)\,PO^5 + 3U^2O^3 + PO^5$, in which the first member is analogous in composition to uranite. The same salt was likewise formed on precipitating a solution of $3NaO + PO^5$ with an insufficient quantity of nitrate of the oxide of uranium.

When so much $3NaO + PO^5$ is added to a solution of the nitrate of uranium that a portion of the precipitate is redissolved, the insoluble residue is a mixture of salts.

On the addition of an equivalent of $3NaO + PO^5$ to one of the nitrate of uranium, a light yellow powder subsided, which on ignition became pale yellowish-green, and retained this colour on cooling. It appeared most probably to possess the formula

$$(U^2O^3, 2HO)\,PO^5 + 3U^2O^3 + PO^5 + xHO.$$

The production of this salt presupposes that the solution of the nitrate of the oxide of uranium contained some free acid.

Arsenic acid forms a similar series of combinations with oxide of uranium, *i. e.* salts with 1, 2, and probably also with 3 atoms of base to 1 atom of acid. The analysis presented the same difficulties. After numerous experiments, the compound was dissolved in muriatic acid, and the arsenic precipitated with sulphuretted hydrogen after converting the arsenic into arsenious acid by boiling with sulphurous acid.

I. *Arseniate of the Oxide of Uranium*, $(U^2O^3, 2HO)\,AsO^5 + 3HO$, is obtained when the nitrate or acetate of the oxide of uranium is evaporated together with an excess of arsenic acid, and dried over sulphuric acid. It separates in yellow crystals, which cannot be

measured, and which when heated in a glass tube part with water, and at a strong red heat with arsenious acid and oxygen, leaving a yellow residue. It is decomposed by water in a similar manner to the corresponding phosphate. It dissolves like the following salts in mineral acids and carbonate of ammonia, and is insoluble in acetic acid and water. The salt lost below 302° 9·2 and 10·8 per cent.; calculated according to the above formula, with 2 atoms of basic water, it should lose 8·91. The analysis of the hydrated salt gave—

Oxide of uranium	48·17	..	1	=47·25
Arsenic acid.....	38·20	..	1	37·92 (As=938·8)
Water	13·70	14·3	5	14·82

II. *Arseniate of the Oxide of Uranium*, $(2U^2O^3 + HO)AsO^5 + 8HO$, is the pale yellow precipitate which is obtained on precipitating acetate or on boiling nitrate of the oxide of uranium with arsenic acid, adding water in the latter case after expelling a great portion of the nitric acid. The salt is insoluble in water and acetic acid, and furnished when heated dense white vapours, water and a greenish residue. At 248° it lost 14·904 per cent. water; 8 atoms correspond to 15·07. It furnished on analysis—

Oxide of uranium.....	59·05	58·7	2	59·40
Arsenic acid.....	23·75	..	1	23·83
Water	17·20	16·6	9	16·77

On the addition of the acid arseniate of potash, $(KO,2HO)AsO^5$ to a solution of the nitrate of the oxide of uranium, a salt was obtained which probably contained 2 atoms of oxide of uranium to 1 atom of arsenic acid, but it could not be procured free from potash.

III. *Arseniate of the Oxide of Uranium and Soda*, $(NaO,2U^2O^3)AsO^5 + 5HO$, separates as a pale yellow powder when a solution of basic arseniate of soda, $3NaO + AsO^5$, is added to one of the nitrate of oxide of uranium. The filtered liquid contains no oxide of uranium. The precipitate must be washed with water containing chloride of ammonium, as otherwise it passes through the filter. When heated it turns reddish-yellow, but resumes its colour on cooling. Boiling acetic acid decomposes it in a slight degree; it removes oxide of uranium, but no arsenic acid. The salt afforded on analysis—

Soda	5·91	1 =	6·420
Oxide of uranium	60·67	2	60·111
Arsenic acid	23·97	1	24·057
Water.....	9·91	5	9·412

The alkalies, especially ammonia, have a great tendency to enter into the composition of this salt.

Analysis of Uranite and Chalcolite.—The method above described of separating phosphoric acid from oxide of uranium by ignition with carbonized tartrate of potash and soda, led the author to repeat the analyses of uranite and chalcolite. The following are the results obtained:—

Chalcolite, $(CuO, 2U^2O^3)PO^5 + 8HO$.

	I.	II.	III.	Mean after deducting the gangue.	Oxygen.	
Oxide of uranium	58·45	57·20	60·80	60·03	9.90	6
Phosphoric acid	15·01	13·52	14·40	14·34	8·03	5
Oxide of copper	..	..	8·27	8·27	1·66	1
Water	15·22	15·55	..	15·39	3·68	8
Earthy constituents	..	0·61	0·22			
Silica	..	..	0·49			

Uranite, $(CaO, 2U^2O^3)PO^5 + 8HO$.

		Calculated according to formula.	Oxygen.	
Baryta	1·03	6·11	0·107	1
Lime	5·86		1·670	
Oxide of uranium	63·28	62·61	10·580	6
Phosphoric acid	14·00	15·58	7·845	5
Water	14·30	15·70	12·710	8

The calculated formulæ placed at the head of these analyses may also be expressed in the following manner, supposing that both the bases of the salts do not saturate 1 equiv. phosphoric acid:—

Chalcolite .... $3CuO + PO^5 + 2(3U^2O^3 + PO^5) + 24HO$.
Uranite ..... $3CaO + PO^5 + 2(3U^2O^3 + PO^5) + 24HO$.

However, the author gives the preference to the first and most simple formulæ, because the examination of the phosphates of the oxide of uranium shows that the phosphoric acid is not completely saturated by 2 equivs. oxide of uranium, all the salts with this number of equivalents moreover containing 1 equiv. basic water; but especially for this reason, that it was easy, by boiling the salt $(2U^2O^3 + HO)PO^5 + 8HO$ with a solution of basic acetate of copper, to prepare artificially chalcolite, $(2U^2O^3 + CuO)PO^5 + 8HO$, in the form of a greenish powder, which exhibited under the microscope exactly the same crystalline form as the mineral.

With respect to the mode of analysing the two minerals, the author observes that they may be treated simply with carbonate of ammonia, which completely decomposes the minerals at the ordinary temperature. From the solution of the two minerals in carbonate of ammonia, to which some chloride of ammonium is added to render the uranite more readily soluble, the phosphoric acid is precipitated with sulphate of magnesia; not a trace of the copper, lime or oxide of uranium is carried down with this precipitate.

Quantitative Determination of the Arsenic.—In the course of his investigations, the author found that a definite compound of arsenic acid with oxide of uranium, $(2U^2O^3 + HO)AsO^5$, insoluble in water, acetic acid, chloride of ammonium, and other saline solutions, was constantly produced upon the addition of acetate of the oxide of uranium to an arseniate with 2 or 3 atoms of base previously acidified with acetic acid. This behaviour, according to the experiments of the author, may be employed to determine arsenic acid,

or arsenic which has been precipitated with sulphuretted hydrogen and oxidized to arsenic acid. The biarseniate of potash gave inaccurate results; but when previously neutralized with potash, it furnished favourable results, as did likewise the neutral and basic arseniate of soda ($2NaO + HO$) AsO^5 and $3NaO\ AsO^5$.

1·312 grm. crystallized arseniate of potash, ($K + 2HO$) AsO^5, was boiled with an excess of potash, then supersaturated with acetic acid mixed with an excess of the acetate of the oxide of uranium, the precipitate washed with a solution of chloride of ammonium (1 part to 16 parts of water), and the chloride of ammonium contained in the precipitate removed by weak spirit (1 vol. water to $\frac{1}{10}$th vol. absolute alcohol). After drying in the water-bath, the yellow precipitate was removed from the filter, which was burnt alone on the lid of the crucible, and the precipitate kept in the crucible for some time at a temperature not quite attaining to red heat. It weighed 2·905 grms. Calculated as $2(U^2O^3)\ AsO^5$, it contains $0{\cdot}832\ AsO^5 = 63{\cdot}41$ per cent. The salt ($KO + 2HO$) AsO^5 requires, according to theory, 63·86. II. 1·718 grm. ($2NaO + HO$) $AsO^5 + 24HO$ were dissolved in water with the addition of acetic acid, precipitated with acetate of the oxide of uranium, and the precipitate washed as above described. It weighed, after heating it, 1·654 grm., and consequently contained $0{\cdot}474\ AsO^5 = 27{\cdot}6$; the soda salt contains, according to theory, 28·61 per cent. III. 1·256 grm. $3NaO + AsO^5 + 12HO$, treated in the same manner as the neutral soda salt, furnished $1{\cdot}17\ (U^2O^3)^2 + AsO^5 = 0{\cdot}333\ AsO^5 = 26{\cdot}51$. According to theory the salt contains 27·11 per cent.

Although this method still requires further examination, it may be stated that to obtain a good result the liquid must contain no ammoniacal salt, otherwise the precipitate will contain ammonia; the acid arseniate must be previously mixed with an excess of alkali, otherwise the whole of the arsenic acid is not thrown down; and lastly, that the liquid must contain no alkaline earth, otherwise this accompanies the precipitate, similar compounds to uranite being probably produced.—*Journ. für Prakt. Chem.*, vol. xliii. p. 321.

On a new and peculiar Substance contained in Œnanthe fistulosa. *By* M. Gerding.

This well-known umbelliferous plant gives off, when rubbed between the fingers in the fresh state, a peculiar narcotic odour. In attempting to isolate the narcotic principle, no result was obtained by distilling with caustic potash; I therefore extracted 20 lbs. of the fresh herb repeatedly with alcohol of 0·863 spec. grav. at the ordinary temperature, and freed the intensely-green extract from chlorophylle, &c. by acetate of lead. The liquid filtered from the green precipitate was of a light yellow colour, and possessed a still more penetrating odour, resembling turnips. The excess of lead was removed from the liquid by sulphuretted hydrogen, filtered, and then evaporated at a gentle heat to within one-eighth of its volume, when a peculiar resinous substance began to separate, which increased on further evaporation, so that the whole was finally converted into a

syrupy, resinous, viscous mass, which amounted from 20 lbs. of herb to between 4 and 5 grms. The blackish-brown substance is somewhat tenacious, has an extremely disagreeable irritating taste, and a very penetrating narcotic odour, which is not easily got rid of from the hands. At 54° F. it is of a tenacious consistence; at a somewhat higher temperature it becomes soft, and begins to melt at 68°. It is not soluble in water, sparingly soluble in alcohol at the ordinary temperature, but perfectly soluble in 12 parts of it between 113° and 122°, equally soluble in acetic acid at the same temperature, sparingly soluble in æther, and insoluble in sulphuric and hydrochloric acid; nitric acid destroys it, producing a red colour. I propose the name of *œnanthine* or œnanthic resin for this resinous substance.

This substance contains nitrogen, as ammonia was evolved on treating it with caustic potash; it was found impossible to crystallize it from alcohol. The alcoholic solution has an acid reaction. It affords with—

Chloride of Platinum, a yellow *crystalline* precipitate.

Perchloride of Mercury, a white precipitate turning gray.

Ammonia, a brown flocculent precipitate.

Potash produces a turbidness, and when added in large quantity separates the resin.

Carbonate of Soda produces a yellowish-brown pulverulent precipitate, as does *carbonate of ammonia*.

Nitrate of Silver causes a considerable reddish-brown precipitate.

Sulphuric Acid precipitates a brown powder, as does also *hydrochloric acid*, only the colour is somewhat more yellow.

A slight excess of ammonia added to a solution of the œnanthic resin in acetic acid produces a brown pulverulent precipitate, which possesses the chemical properties of the substance above described, but is not resinous. To this substance the author gives the name of *œnanthine*, and supposes it to be combined in the œnanthic resin with an acid; since on the distillation of an alcoholic extract of the resin, resin constantly separates in the retort during the operation, whilst above the level of the liquid a whitish ring is deposited, which is volatilized and passes into the distillate. This forms a white, milky, faintly-acid liquid, with an odour similar to the œnanthic resin, but considerably milder and more agreeable. The author supposes it to contain a volatile acid, but was prevented, from want of material, from extending his inquiries further on the subject. It has a powerful effect upon the animal system; half a grain administered to a full-grown person produces a long-continued irritation in the palate, followed by a hoarseness of two to three hours' duration; one grain sufficed to produce a slight vomiting. It may therefore prove interesting in a therapeutical point of view.—*Journ. für Prakt. Chem.*, July 15, 1848.

On some Salts of Dithionous (Hyposulphurous) Acid.
By F. Kessler.

Dithionite of Potash has hitherto been obtained in four different forms. Rammelsberg examined a salt with the composition

$3(KO, S^2O^2) + HO$, Döpping the two salts $KO, S^2O^2 + HO$ and $2(KO, S^2O^2) + 3HO$, and Plessy the salt $KO, S^2O^2 + 2HO$. No anhydrous crystallized compound is known. The author has again examined the salts of potash, and has moreover described several other earthy dithionites and some double salts. Döpping obtained the two above-mentioned salts by treating the pentasulphuret of potassium with neutral chromate of potash. The decomposition must be as follows:—

$$2KS^5 + 8KO, CrO^3 = 5(KO, S^2O^2) + 4Cr^2O^3 + 5KO.$$

The liberation of potash, which occurs in this reaction, may be avoided, according to the author, by employing the bichromate of potash instead of the neutral chromate, when the following decomposition takes place:—

$$2KS^5 + 4(KO, 2CrO^3) = 5(KO, S^2O^2) + 4Cr^2O^3 + KO.$$

If the salt be prepared according to this method, the hot solution of the chromate should be added to the hot solution of the sulphuret of potassium, taking care that the eliminated oxide of chromium has assumed a pure green colour before any further addition is made. If, on the contrary, the solution of the pentasulphuret of potassium is poured into that of the bichromate of potash, only brown oxide of chromium and sulphate of potash are obtained.

Dithionite of Potash, $3(KO, S^2O^2) + HO$ (air-dried), was obtained according to the above method; the solution was evaporated at 86° F., when the salt separated in thin prisms. The amount of water was determined by drying it at 212°. Analysis gave—

Potash	47·60	..	3 =	48·02
Dithionous acid	..	49·29	3	48·92
Water	4·20	..	1	3·06

Dithionite of Potash, $3(KO, S^2O^2) + 5HO$ (air-dried), was obtained from the mother-ley of the preceding salt. When nothing further separated on cooling, it was shaken violently, when small granular crystals were deposited; these were again dissolved in the mother-ley by a gentle heat and the addition of some water, when upon cooling large colourless crystals (rhombic octahedrons) separated. Some more of the same salt was obtained on evaporating the mother-ley. The salt parted with its water over sulphuric acid; that employed for analysis II. was dried at 356°:—

	I.	II.		
Potash	42·62	..	42·45	3 = 42·79
Dithionous acid	..	..	..	3 43·59
Water	..	13·73	13·47	5 13·62

The two preceding salts may be obtained at will from a solution of dithionite of potash. A solution of hyposulphite of potash, prepared by boiling sulphite of potash with an excess of sulphur, was divided into three portions; one of these afforded, on evaporation at 86°, a confused crystalline mass of prisms; the second portion was likewise evaporated at 86°, the mother-ley poured off the prismatic crystals, allowed to cool, and then well shaken. This pro-

duced a finely-granular precipitate, which after being redissolved deposited large octahedral crystals. One of the octahedral crystals was conveyed into the third portion when it had cooled down to 86°. After some time crystals of the same form separated. From the mother-ley in which crystals of this form have once separated more are readily obtained on concentration.

It results from this, and from the nature of the other salts of dithionous acid which have been accurately examined, that they contain less water of crystallization when they have been crystallized at a high temperature.

The salt obtained in the manner just mentioned forms perfectly colourless octahedrons of considerable lustre, which do not deliquesce in a moderately-moist atmosphere. They effloresce at 104° and over sulphuric acid; they dissolve in water, producing a considerable degree of cold; the solution is neutral, and is not decomposed by exposure to the air. The analyses of the salt agree with the last-mentioned, as will be seen by the following numbers:—

Potash	42·84	42·84	..	..	3	=42·79
Dithionous acid....	44·16	43·67	43·82	43·70	3	43·59
Water.....	13·32	13·53	..	..	5	13·62

This is the salt which Döpping has described as deliquescent and of a yellow colour, with the formula $2(KO, S^2O^2) + 3HO$. The numbers which he found agree best with the author's formula $(KO, S^2O^2) + 5HO$. The yellow colour is owing to the presence of a trace of chromate of potash, and its deliquescence to an admixture of carbonate of potash. The author is of opinion that the salt described by Plessy as $KO, S^2O^2 + 2HO$ also belongs here.

Including Rammelsberg's salt, we have therefore the following dithionites of potash:—$3(KO, S^2O^2) + HO$; $KO, S^2O^2 + HO$; $3(KO, S^2O^2) + 5HO$.

Dithionite of Potash and Percyanide of Mercury, $KO, S^2O^2 + HgCy$ (dried over sulphuric acid).—Percyanide of mercury produces no precipitate in a solution of dithionite of potash, which the other salts of mercury do; but they assume an alkaline reaction, owing probably to the formation of cyanide of potassium. A solution containing percyanide of mercury and hyposulphite of potash in equivalent proportions deposits, on evaporation by heat or in the cold, and likewise on the addition of alcohol, a mixture of small laminæ and granular crystals, which could not be separated. The following double salt was obtained only once on evaporating *in vacuo* the mother-ley of the mixture precipitated with alcohol. It formed large four-sided prisms, which dissolve more readily than the mixture of the two salts precipitated by alcohol. When merely dried between paper, the crystals become in a few days yellow and opake, and smell of hydrocyanic acid; over sulphuric acid they lose 2 per cent. of water, and are then no further decomposed. Heated in a glass tube, this salt melts, giving off sulphurous acid, cyanogen, mercury and sulphuret of mercury, but no water; the residue consists of sulphuret of potassium and sulphate of potash. Dried over sulphuric acid, the salt afforded on analysis—

Potash	21·14	..	21·90	1	=21·32
Dithionous acid.....	..	22·21	23·99	1	21·71
Percyanide of mercury	..	56·30	55·51	1	56·98

Dithionite of Strontia, $SrO, S^2O^2 + HO$, is very easily obtained by mixing hot concentrated solutions of 7 parts of nitrate of strontia and 6 parts of dithionite of soda; on slow cooling nearly the whole amount of the strontia salt separates. On passing sulphurous acid into a solution of sulphuret of strontium, great loss occurs, owing to the production of sulphite of strontia. According to Rammelsberg, the salt contains 5 atoms of water of crystallization, 6 per cent. or nearly 1 atom of which is held back after drying at 356°. The salt with 1 atom of water is obtained directly by evaporating the solution at 122°. It afforded on analysis—

Strontia	47·60	1	= 47·67
Dithionous acid	..	1	44·07
Water	..	1	8·26

Dithionite of Lime was obtained by dissolving 2 parts of crystallized chloride of calcium, CaCl + 6HO, and 8 parts of hyposulphite of soda in hot water; the solution was evaporated at 122°, decanted from the chloride of sodium which had separated, and the temperature lowered to 86°, when crystals of pure dithionite of lime separated.

Dithionite of Magnesia and Potash is obtained by mixing hot concentrated solutions of sulphate of magnesia and hyposulphite of potash in equivalent proportions. On cooling, nearly the whole of the double sulphate separated, and on further evaporation the dithionite. By placing a crystal in the concentrated ley, large crystals may be obtained, which melt below 212° with the separation of sulphur.

Dithionite of Magnesia and Ammonia, $NH^4O, MgO + 2S^2O^2 + 6HO$, is obtained by the decomposition of the double sulphate with dithionite of strontia. The concentrated solution is soon rendered turbid by heat; crystals separate from it below 32°, which easily deliquesce. Analysis afforded—

Ammonia	..	..	..	1	= 13·26
Magnesia	9·92	9·28	..	1	10·24
Dithionous acid	..	..	48·25	2	48·96
Water.....	..	..	..	6	27·96

Poggendorff's *Annalen*, June 1848.

Analysis of the Cyanide of Lead. By L. Kugler.

According to the author, the yellowish-white precipitate which is formed when basic acetate of lead is precipitated with prussic acid and the addition of ammonia, is represented by the formula

$$PbCy + PbO + HO.$$

Liebig's *Annalen*, lxvi. p. 63.

Observations on Sulphurous Acid and its Combination with Water.

By J. I. Pierre.

It is generally admitted in works on chemistry that the hydrate of sulphurous acid does not crystallize readily in the moist way; it is easy however to ascertain by experiment, that when a current of sulphurous acid gas, previously washed, is passed into a concentrated solution of this gas, taking care to keep the flask containing the solution at a temperature very near to 32°, a crystalline deposit is soon seen to form, which increases very rapidly if the current of gas is continued. In this manner several hundred grms. of these crystals may be obtained in a few hours.

When large crystals are desired, the conducting tube must not be immersed in the liquid, as it would cause an agitation unfavourable to crystallization. Beautiful transparent crystals are equally obtained by exposing a highly concentrated solution of sulphurous acid to a temperature a little above 32°.

The crystals of the hydrate of sulphurous acid contain more than 28 per cent. of acid instead of 20, as generally admitted according to the analysis of M. De la Rive made with a product obtained in the dry way, and not regularly crystallized. The formula which appears best to represent its composition is $SO^2, 9HO$*.

These crystals contain about four times as much sulphurous acid as a concentrated solution of the gas at the ordinary temperature and pressure. When exposed to a temperature above 40°, they melt and part with a portion of their acid. When projected into a platinum crucible heated to between 76° and 86°, they produce a noise comparable to that of a red-hot iron suddenly immersed in water. When well-drained, these crystals withstand the action of the atmosphere much longer than the solution of sulphurous acid.

The accurate analysis of these crystals presented several difficulties. The process which I followed consisted in weighing approximatively a certain quantity of the crystals previously dried upon cold bibulous paper, then placing them in a dry atmosphere of sulphurous acid at a temperature lower than the melting-point of the crystals, but higher than the freezing-point of water. After a few minutes the proper quantity is weighed off, which may be done with great rapidity, the approximative weight being known; the crystals are then emptied into a concentrated cold solution of chlorine, and the sulphurous acid estimated in the state of sulphate of baryta.

It may perhaps not be wholly without interest to describe the unsuccessful attempts which I made to obtain a hydrate containing more acid. Anhydrous sulphurous acid does not dissolve any quantity of water under the ordinary pressure; between 14° and 10° a snow-like substance, it is true, is obtained, which appears to consist of a mixture of frozen water and the preceding hydrate; but the portion which remains liquid contains but mere traces of water. If some water is enclosed with an *excess* of anhydrous sulphurous acid

* Compare the observations of M. Döpping on this subject, communicated in our last Number, p. 320.—Ed. *Chem. Gaz.*

in a tube sealed before the blowpipe, and the tube is then exposed to a temperature of 50°, 54°, 59°, 68°, or even 77°, however much the two liquids may be agitated to mix them, they always separate in a few moments into two distinct layers, of which the first and upper one is a concentrated aqueous solution of sulphurous acid, while the lower stratum contains but insignificant traces of water, even though the experiment has been continued several months. The author considers that this minute quantity of water is adherent to the sides of the tube and not held in solution by the acid, as the surface of separation of the two liquids is convex, which appears to indicate greater affinity between the water and the glass than seems to exist between the water and the acid.—*Comptes Rendus*, July 3, 1848.

On the Acid contained in the Leaves of Ilex Paraguayensis.
By Dr. F. Rochleder.

The leaves of this plant, known under the name of Paraguay tea, are used in South America in the same manner as tea in Europe and several countries of Asia. Stenhouse has found that the crystalline substance contained in it is identical in its composition and properties with caffeine. To ascertain the nature of the acid which accompanies the caffeine in Paraguay tea, and furnishes the material for its formation, I examined a small quantity of the tea in the following manner:—The tea was rubbed to a powder, and exhausted in a stoppered vessel with alcohol of 0·951 spec. grav., which after some hours was replaced by a fresh quantity as long as it acquired a yellow colour. The yellow solution was precipitated with an alcoholic solution of acetate of lead, as long as the precipitate exhibited a somewhat dirty-yellow colour. This, separated by filtration, dries to a dark greenish-brown mass. The yellow filtered solution is now entirely precipitated with an alcoholic solution of acetate of lead, and the beautiful yellow precipitate washed with alcohol upon the filter, suspended in alcohol, and decomposed with sulphuretted hydrogen. After expelling the excess of sulphuretted hydrogen, the liquid was poured into a large quantity of a solution of acetate of lead in alcohol, the precipitate washed with alcohol, and dried at 212°. This lead salt afforded on analysis the following numbers:—

Carbon	22·84	14	= 1050	22·63
Hydrogen	2·20	8	100	2·15
Oxygen	15·64	7	700	15·10
Oxide of lead.....	59·32	2	2789	60·12

Deducting the amount of oxide of lead, there remains for the acid C 56·1, H 5·4, O 38·5, which is the composition of caffeo-tannic acid.

To convince myself of the identity of these two acids, I decomposed a portion of the lead salt which had been employed for the above analysis with sulphuretted hydrogen. The solution filtered from the sulphuret of lead was slightly yellow, acquired a dark reddish-yellow colour with ammonia, potash or soda, and was coloured

dark green with perchloride of iron. Mixed with an excess of ammonia and exposed to the air, the liquid became dark green, which colour was converted into brown by the addition of acetic acid. The brown acid liquid afforded with a solution of acetate of lead a dark blue precipitate, which was coloured red by sulphuric acid. All these reactions agree with those presented by caffeo-tannic acid under the same circumstances; consequently the identity of the acid contained in the leaves of *Ilex Paraguayensis* with that existing in the berries of coffee is proved.—*Ann. der Chem. und Pharm.*, lxvi. p. 39.

Observations on the Sulphovinates. By Prof. R. F. Marchand.

The facility with which the sulphovinates are decomposed surpasses most of the salts of the other acids conjoined with sulphuric acid. The sulphonaphthalates may be preserved for any length of time unaltered, and will bear a high temperature before they are decomposed; the sulphobenzoates and the sulphobenzidates may be exposed to a very high temperature without any change; even the phosphovinates are much more stable than would be expected from their analogy with the sulphovinates. It is owing to the readiness with which the sulphovinate of baryta is decomposed when heated to nearly the boiling-point of water, that the compositition of the acid remained for a long time in doubt.

I have kept a considerable number of sulphovinates for twelve years; some were wholly unaltered, while others were entirely decomposed. The potash, soda, ammonia and lithia salts had experienced no change; their solutions were not acid, nor could the presence of sulphates be detected in them. Of the salts of the alkaline earths, only that of magnesia had remained unchanged; and of the salts with metallic oxides, those of copper, nickel, cobalt and zinc.

The salt of strontia was the first to be decomposed; the crystals of the baryta salt were still perfectly transparent, whilst this had already become coated with an acid liquid, and diffused an agreeable vinous odour. The whole of the strontia was soon converted into sulphate.

The baryta salt was next in succession. No baryta was found in the solution, and the liquid contained a mere trace of an organic substance combined with sulphuric acid; it was not sufficient to ascertain its composition and to determine whether free sulphovinic acid existed in it or a similar combination had been formed. On boiling a solution of sulphovinate of baryta, sulphate of baryta is constantly deposited for a certain time, and the liquid becomes acid. If it is neutralized and boiled again, a point is at last attained at which the solution of the baryta salt is no longer decomposed. On evaporation crystals separate from it, which have the same composition as the sulphovinate of baryta. The salt which had been dried under the air-pump over sulphuric acid was analysed; 1·228 grm. left on ignition 0·739 sulphate of baryta = 60·1 per cent.; theory requires 60·07. Nevertheless this salt does not appear to be the

sulphovinate of baryta. The same observation has been made by Gerhardt, who likewise considers the salt to be distinct from the sulphovinate.

The sulphovinate of lime was not completely decomposed; it keeps best when free from adherent moisture.

The sulphovinates of alumina, peroxide of iron, protoxide of manganese, oxide of uranium, lead and silver were wholly decomposed. No etherole could be obtained from the acid liquid.—*Journ. für Prakt. Chem.*, vol. xliv. p. 122.

Analyses of Calcareous Sea-sand, Felspar and Corallines from the Coast of Devonshire. By THORNTON J. HERAPATH*, Esq.

The calcareous sea-sand which collects in vast quantities in many parts of the Devonshire and Cornish coasts is, as is well known, most extensively employed by the agriculturists of those counties as a manure. In such high estimation indeed is this sand held, that many thousands of tons of it are annually conveyed from the sea-side to be applied to the lands in the interior. It is generally preferred by the farmers to cart it away directly after the receding of the tide, when it is completely saturated with the sea-water, the salts of which must of course materially increase its value as a manure. It has been found by them to produce the most beneficial effects on close clayey soils, which it opens and renders more porous, and thus enables the water and atmospheric air to have a freer access to the roots of the plants, and at the same time facilitates the drainage of the land.

The sand which I subjected to analysis was obtained from Barracaine, a small cove within a few miles of Ilfracombe. It contained in 100 parts—

Water	0·500
Soluble salts, consisting chiefly of chloride of sodium, sulphates of soda and magnesia, with minute traces of potash	0·300
Organic matter	2·420
Carbonate of lime	47·438
Carbonate of magnesia	0·097
Sulphate of lime	very minute traces
Phosphate of lime	0·025
Oxide of iron Alumina	0·460
Sand, silica and *débris* of slaty and granitic rocks	48·760
	100·000

20 grs. of the sand burnt with potash and lime gave of ammonio-chloride of platinum 0·58 gr.=0·1845 per cent. of nitrogen=0·2240 gr. of ammonia.

The traces of potash observed in the soluble salts were with-

* Communicated by the Author.

out doubt derived from the decomposition of the felspar, of which a pretty large proportion of the substances insoluble in hydrochloric acid consisted. This felspar would become gradually disintegrated by the combined influences of air and moisture, and yield up its potash to the soil, which it would improve to that extent, rendering it better suited for the cultivation of grain crops.

A fine specimen of this mineral, from the same locality, was found upon analysis to consist of—

Silica	64·109
Alumina	19·013
Lime	0·500
Magnesia	very minute traces
Oxide of iron	traces
Potash	16·277
	99·899

By acting upon some of the same felspar, partially decomposed and in fine powder, with boiling hydrochloric acid, &c., as recently proposed by Fownes*, I was enabled to verify the statement of that gentleman with regard to the presence of phosphoric acid in this mineral. Evident traces of the acid could be detected in the solution from 500 grs. of the powdered mineral.

The carbonate of lime and magnesia and phosphate of lime contained in the sand is principally derived from comminuted shells and corallines, as may be easily proved by an ocular examination.

Some specimens of corallines from Budleigh Salterton, on the same coast, were found to contain in 100 grs. as follows:—

Soluble salts	traces
Organic matter	9·040
Carbonate of lime	84·257
Carbonate of magnesia	1·373
Sulphate of lime	traces
Phosphate of lime	0·100
Oxide of iron	0·820
Silica and sand	2·400
Fluoride of calcium	minute traces
Water and loss	2·010
	100·000

20 grs., when burnt with potash and lime, gave of ammonio-chloride of platinum 2·17 grs. = 0·689 per cent. of nitrogen, or 0·837 gr. of ammonia.

These corallines are now very largely employed in commerce in the manufacture of Barker's patent submarine manure, of which they form one of the principal constituents.

Previously to mixing them with the sea-weed, night-soil, decayed fish, &c., which compose the remaining ingredients of this manure,

* Phil. Trans. for 1844, p. 53 *et seq.*

they are heated with about an equal quantity of common salt, which effectually disintegrates them, and renders their constituents in a more fit state to be assimilated by plants.

Mansion House, Old Park, Bristol, Aug. 23, 1848.

On the Presence of Phosphate of Lime in Basaltic Rocks. *By* Isaiah Deck, *Chemical Assistant in the Gottingen Laboratory**.

The presence of phosphoric acid in igneous rocks has been freely asserted by Prof. Fownes, and as equally disputed by Prof. Kersten†.

During a geological ramble to the Blaue Kappe, or Blue Point Mountain, near Eschwege, Hessia, a short distance from, and forming part of, the range of the Meissner, from the basalt of which Kersten derived the samples which he experimented upon, I discovered in a mass of compact basalt a mineral which in its colour and prismatic crystals closely resembled apatite, and upon subsequent analysis yielded a large quantity of phosphate of lime, with traces of fluoride and chloride of calcium, thus $Ca\left\{\begin{matrix}Cl\\Fl\end{matrix}\right. + 3Ca\dddot{P}^3$, which closely approximates the formula for apatite.

I trust that this will set at rest the disputed point, and thoroughly establish Mr. Fownes's views. I would also remark that apatite is found abundantly in the hornblende rock of Ahrendahl in Norway, a rock of undoubted igneous origin.

On the Formation of Urea and Sulphocyanogen from Fulminic Acid. *By* Dr. J. H. Gladstone.

Gay-Lussac and Liebig were led to assume, from their investigation on fulminic acid, that urea would probably be formed from the fulminate of copper and ammonia on removing the copper with sulphuretted hydrogen; no experiment however was made to affirm this supposition. Wöhler's discovery, that urea may be artificially produced by the union of cyanic acid and ammonia, rendered the above assumption highly probable. But since recently the relation previously supposed to exist between fulminic acid and the cyanogen series has been denied, it appeared desirable to ascertain the fact experimentally. For this purpose fulminate of silver was mixed with a quantity of water, and placed in contact with metallic copper, and thus a soluble fulminate of copper obtained. The decanted liquid was then mixed with a large excess of ammonia, which displaced half the copper and furnished a fulminate of copper and ammonia. A current of sulphuretted hydrogen was now passed into this, which precipitated the whole of the copper, and produced urea and sulphocyanic acid. After having separated the precipitate, the latter was removed in the state of a basic salt of lead, when, on concentrating the liquid, crystals of pure urea were obtained. The author has furnished several analyses in support of this

* Communicated by the Author.

† Chem. Gaz., vol. iii. p. 298.

interesting metamorphosis, which may be expressed in the following manner:—

$$Cu\,C^4\,N^3\,H^4\,O^4 + 3HS = CuS + C^2\,N^2\,H^4\,O^2 + C^2\,NHS^2 + 2HO.$$

Ann. der Chem. und Pharm., April 1848.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of pure Sulphuric Acid. *By* Aug. A. Hayes.

In the arts, the rapid extension given to refined operations has led to the consumption of pure chemical products. Applications of such substances as were formerly only in the hands of accurate chemists, are now of daily occurrence in manufacturing. The want felt for pure sulphuric acid has to a certain extent been supplied by the Nordhausen acid; but independently of a higher price restricting its consumption, the manufacture is foreign to this country.

Without entering into scientific details, I shall describe an œconomical process, which I have carefully studied, and by which the pure acid used in my laboratory has long been obtained.

In the manufactories of sulphuric acid, the weaker acid from the lead chambers is concentrated in lead pans, usually to the density of 1·76, and transferred without cooling to the platinum alembics for further concentration.

The modification commences with the hot acid, and it may be supposed to contain sulphurous acid, hydrochloric acid, hyponitric acid, arsenious acid, oxides of iron and lead, alumina, lime, soda and organic matter, although the acid obtained from the combustion of Sicily sulphur is rarely thus impure. On adding to the hot acid sufficient nitrate of potash or soda to destroy the organic matter, the brown colour disappears, and the fluid becomes colourless. The addition of $\frac{1}{300}$th of sulphate of ammonia removes the remaining hyponitric acid; much of the hydrochloric acid has been removed by the nitrate, and sulphurous and arsenious acids carried to their highest stage of oxidation. The oxides present aid the further purification; by continuing the concentration to 1·78, a trifling addition of oxide of lead is made; but it is essential to the success of the process that this point of density be reached. The fluid must now be cooled in deep vessels of lead, the temperature of it being gradually reduced to 32° F., and allowed to become perfectly clear. The clear part must then be run into shallow lead vessels, so placed that they may be refrigerated to 0° F. As the whole acid has nearly the hydrate composition of $SO^3 + 2HO$, it would form by repose a solid crystalline mass. In ordinary cases the regular crystals form solid masses, which are allowed to increase till one-half the bulk of the fluid has assumed the solid state, when the remaining liquor is rapidly removed, the crystals broken up, and washed with some acid resulting from the crystals of a former operation.

When crystallized in this way, nearly all the contamination which can be detected arises from the fine granular sediment of anhydrous sulphates and arseniates of iron and lead mixing with the crystals from careless washing. These substances are deposited in the cooling, but more abundantly in the course of the crystallization of this acid. The crystals melted in lead kettles which have been recently washed with ordinary sulphuric acid, afford an acid nearly pure; and if required in the concentrated state, may be transferred directly to the platinum alembic, melted and boiled. For the most delicate researches, the crystals must be melted in glass or stone-ware recrystallized out of contact with metals or dust, leaving one-half or one-third of the acid in a fluid state. If the subsequent use of the acid does not require the removal of the water, which is very rarely the case, the crystals, being a perfectly definite hydrate when fluid, enable us to weigh and apportion the quantity of real acid with great precision.

In the laboratory, when used for cases of difficult decomposition, it may be added to the crystallized bisulphate of potash, mixed with the substance to be acted on, and the whole brought to any state of dryness in the platinum utensils employed in such operations.

All the acid from which the pure acid has been abstracted may be used for generating nitric or hyponitric acid in the manufacture of sulphuric acid. The manufacture may best be carried on during the winter months, and the crystals obtained stored or melted.

This hydrate is remarkable for the regularity and great size of its crystals. They are oblique four-sided prisms, and often present faces of twelve by sixteen inches. Their capacity for heat is also surprising; small parcels exposed at the mean temperature of 46° F. melt with extreme slowness.—Silliman's *Journal*, July 1848.

Notice respecting a new Process for Etching upon Copper and Steel. *By* Dr. H. Schwartz *and* Dr. R. Böhme.

The method of etching employed by copper- and steel-plate engravers has hitherto depended upon the use of more or less dilute nitric acid. The consequent disengagement of nitric oxide gives rise to several inconveniences; sometimes the bubbles of gas adhering to the metal, and so protecting certain portions from the action of the acid, required constant attendance and a continual removal with the pencil, to prevent the lines from being very unequal; moreover, this liquid exhibits a tendency, which has hitherto been left unexplained, of eating away the margins, so that it is very difficult to obtain lines of any fineness sufficiently deep. Again, the action is frequently hastened more than is desirable by the absorption of the nitrous acid formed from the nitric oxide. This evil might have been obviated by the addition of urea much better than by creosote. In the next place, the large amount of nitrous acid disengaged affects the chest considerably. It was therefore desirable to discover some solutions which might serve the same purpose without being accompanied by the inconveniences above alluded to.

This object appeared to us most easily obtained by the use of halogens, which combine directly with the metals. Some experiments on a small scale furnished the desired results:—

Liquid for etching upon Copper.—Take 10 parts of fuming muriatic acid of commerce (containing 40 per cent. of dry muriatic acid), dilute it with 70 parts of water, and add to it a boiling solution of chlorate of potash in 20 parts of water. We thus obtain a solution which contains, so to say, a considerable amount of disposable chlorine. This may now be diluted with 100 or 200 parts of water, to bite in the fainter portions. The deep tints are produced by length of time or by the addition of stronger liquid. The faint odour of chlorine is by no means so disagreeable as the vapours of the nitrous acid.

Liquid for etching Steel.—Take 2 parts of iodine and 5 parts of iodide of potassium, and dissolve both in 40 parts of water; this is the strongest liquid. It may be diluted with 40 parts of water to etch the faintest lines. The deeper tints are produced by length of time or stronger liquid.

The lines so produced are very deep, extremely well-defined, with perfectly straight margins, and even the finest lines drawn with the ruling-machine quite close to one another remain perfectly distinct. On account of the slow action, there is no occasion for hurry. The liquid which has been used should not be thrown away, on account of the high price of the iodine; it may be filtered, and again rendered active by the addition of some chlorine-water.—Liebig's *Annalen*, lxvi. p. 63.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Swansea, August 9th, 1848.

The following are abstracts of the principal communications brought before the Chemical Section, as reported in the *Athenæum*:—

On the Colouring Matters of Madder. By Dr. Schunck.

On treating finely-ground madder roots with boiling water, a brown fluid is obtained having a taste between bitter and sweet. In order to extract all the substances capable of solution in water, about sixteen quarts of water are required for every pound of madder. To this fluid any strong acid, such as sulphuric or muriatic acid, is added in slight excess. Nitric acid must not be used for the purpose. Oxalic acid is best adapted, as it can afterwards be completely removed by chalk. The acid produces a dark brown precipitate, which is separated by filtration, and washed with water until the excess of acid is removed. The percolating fluid is yellow. This brown precipitate consists of seven vegetable sub-

stances, viz. alizarine, rubiacine, alpha-resin, beta-resin, rubian, pectic acid and oxidized extractive. The examination of the fluid was next made; it was found to contain xanthic acid, madder-yellow and sugar. The continued investigation of the subject has led to the conclusion that there is but one colouring matter in madder, *i. e.* the alizarine; and that the substance which was thought to be a colouring matter, viz. rubiacine, is not so.

It is known that after madder has been employed for dyeing, it still contains colouring matter, and that the article garancine is manufactured from this. By treating this substance with boiling muriatic acid, it was found to contain lime, magnesia, oxalate of lime, phosphate of lime, alumina and peroxide of iron. After these salts were separated, boiling water extracted a large quantity of colouring matter, which would dye mordanted cloth quite full, and of the same colour as madder itself, thus showing that it contains alizarine. Alizarine is found to be composed of—

Carbon	56·97
Hydrogen	4·19
Oxygen	38·84

or, in fact, of carbonic acid and water. Alizaric acid is formed by treating alizarine with concentrated persalts of iron or nitric acid. The salts of this acid are mostly soluble. Alizarate of lime is prepared by neutralizing alizaric acid with carbonate of lime, and evaporating to crystallization. It crystallizes in prisms possessing great brilliancy. Alizarate of baryta, prepared in the same way by means of carbonate of baryta, crystallizes in silky needles. Alizarate of silver, prepared by double decomposition, is soluble in boiling water, from which it crystallizes as the solution cools. Alizarate of lead is insoluble. By subjecting alizaric acid to heat, it is volatilized, and forms a sublimate in the shape of long white needles, to which the name of pyro-alizaric acid is given. By solution in water, pyro-alizaric acid appears to be again converted into alizaric acid. Rubiacine was found to be $C^{31} H^{9} O^{10}$, and rubiacic acid $C^{31} H^{9} O^{16}$. Alpha- and beta-resin were next examined, as were also the other constituents; and the author then proceeded to examine the part which each material plays in the process of dyeing; from which it is satisfactorily proved that alizarine is the substance producing colour; and the advantages of converting madder into garancine consist in removing the resins and those bodies which are not only useless but injurious, and in separating alizarine from those salts with which it exists in the madder root in close combination.

On the advantageous Use made of the Gaseous Escape from the Blast Furnaces of Ystalyfera. By Mr. J. Palmer Budd.

This communication drew attention to an œconomical application of the heated gases which are usually allowed to escape from the top of the iron furnaces. It appears that the gases which are evolved from these furnaces escape at a temperature which is about the melting-point of brass. In the iron works at Ystalyfera, where the

iron is smelted by the use of anthracite coal, advantage has been taken of this in a most ingenious manner. By an arrangement, which is in its character exceedingly simple, the hot gas is led off into another channel by means of a strong current generated through a chamber and air-way from a point just below the top of the iron furnace. It is conducted, very little heat being lost in the passage, under the boiler of a steam-engine; and it is found to be at a sufficiently high temperature to heat the boiler without the consumption of any fuel whatever. Hence an immense saving is effected. Although only one furnace and one boiler have hitherto been adapted to this purpose, it is found to effect a saving of 350*l.* a-year. We may consequently expect, that when the experiment is further extended, and more of the furnaces so arranged that this heat may be œconomized and employed for the numerous useful purposes to which it is applicable in a large establishment, the saving will amount to many thousands annually.

On the Alloys of Tungsten with Copper and other Metals. *By* Dr. Percy.

Since the introduction of some processes by which tungsten has been separated from its ores, and from its combinations with tin and other metals in nature, numerous experiments have been made with the hope of employing it usefully. From the peculiar nature of tungsten, it has been thought that it would have the property of giving greater hardness to the metals with which it might be alloyed, and also of protecting them from oxidation. It was with this hope that Dr. Percy made an extensive series of experiments, alloying copper, brass, German silver, and other metallic bodies, with tungsten. In no case, however, has the result been of a satisfactory character.

Analysis of Wrought Iron produced by Cementation from Cast Iron. *By* Prof. Miller.

The results of analysis were briefly these:—The quantity both of carbon and silicon is materially diminished by the cementation, though still the proportion of both is materially greater than in good bar iron. It also appears that the portion of carbon which is insoluble in acids is nearly the same both before and after the iron has been rendered malleable, the diminution being confined almost to that portion of carbon which was chemically combined with the metal, and which therefore would be in a state for propagation through the mass more readily by cementation.

On some Properties of Alumina. *By* R. Phillips, F.R.S.

It has been observed by Wittstein, that the precipitate which is obtained from the persulphate or perchloride of iron, if kept for a great length of time in water, loses almost entirely the property of being soluble in acetic acid. Mr. Phillips had noticed a similar phænomenon with alumina, arising without doubt from the action of the

cohesive forces. Whereas the sesquioxide of iron requires one, or probably two years, for the production of the effect, alumina undergoes the change partially in a very short time, the precipitated alumina does not however assume a crystalline appearance, stated to be the case with the cohering sesquioxide of iron. If the precipitated alumina is kept for two days moist or in the solution from which it was precipitated, even sulphuric acid does not immediately dissolve it. A number of experiments were brought forward in proof of this fact. It was also shown that the interposition of magnesia or of carbonic acid prevented the alumina from cohering.

On the peculiar cooling Effects of Hydrogen and its Compounds in Cases of Voltaic Ignition. By W. R. Grove, Esq.

This communication was illustrated by an experiment, in which it was shown that a platina wire, rendered incandescent by a voltaic current, was cooled far below the point of incandescence when immersed in an atmosphere of hydrogen gas. This remarkable cooling property of hydrogen of course became the subject of experimental examination in comparison with other gaseous media. By a very ingenious arrangement, tubes containing coils of platinum wire were filled with hydrogen and other gases, and then being plunged into water in which delicate thermometers were placed, the wires were traversed by the same current from the battery; and it was found that the water was always more heated in a given time by the wire in the tubes of oxygen, nitrogen, carbonic acid, carburetted hydrogen, &c., than by that in the tube containing pure hydrogen. It became necessary now to ascertain the cause of this peculiar phænomenon of hydrogen. It was found not to be due to specific heat, nor to the conducting powers of the gases. Convection did not explain the fact; and considerable difficulty was found upon examination to exist if it was attempted to refer it to the greater mobility of the particles of hydrogen gas, the lightest known, than of either oxygen, nitrogen or carbonic acid. It was found that this peculiar property also belonged, but to a less extent, to all the compounds of hydrogen and carbon.

In the discussion which followed, Prof. Graham mentioned the curious fact, observed by him in his researches on the diffusion of gases, that the hydrocarbons move through tubes with great velocity; and that æther vapour, which is four times the density of hydrogen, moves, notwithstanding its weight, at four times the rate of other gases. It was thought this would perhaps serve to indicate the path in which an explanation might be looked for.

On a peculiar Property of Coke. By Mr. J. Nasmyth.

The following interesting fact was discovered some years ago, and it appears to furnish additional evidence as to the identity of the diamond with carbon, namely, that *coke* is possessed of one of the most remarkable properties of the diamond, insofar as it has the property of *cutting glass.* I use the term "cutting" with all due consideration, in contradistinction to the property of scratching, which

is possessed by all bodies that are harder than glass. The *cut* produced by coke is a perfect, clear, diamond-like cut, so clean and perfect as to exhibit the most beautiful prismatic colours, owing to the perfection of the incision. Coke hitherto has been considered as a soft substance, doubtless from the ease with which a mass of it can be crushed and pulverized; but it will be found that the minute laminar crystals, of which a mass of coke is composed, are *intensely hard*, and as before said are possessed of the remarkable property of *cutting* glass. This discovery of the extreme "diamond-like" hardness of the particles of coke will no doubt prove of value in many processes in the arts, as well as interesting in a purely scientific sense.

On common Salt as a Poison to Plants. By W. B. Randall.

The following notice is presented as being likely to afford a useful practical caution to those interested in the cultivation of plants. In the month of September last, three or four small plants in pots were shown to the writer, nearly or quite dead; and he was at the same time informed that their destruction was a complete mystery to the party to whom they belonged, and that Dr. Lindley had expressed his opinion, from the examination of a portion of one sent to him, that they were poisoned. Having searched in vain for any strong poison in the soil, and in the plants themselves, he inquired more minutely into the circumstances of the case, and found that these were only specimens of many hundreds of plants both in the open air and in green-houses (but all in pots), which exhibited, in a greater or less degree, the same characteristics. The roots were completely rotten, so as to be easily crumbled between the fingers; the stems, even in young plants, assumed the appearance of old wood, the leaves became brown, first at the point, then round the edge, and afterwards all over; while the whole plant drooped and died. At least 2000 cuttings, in various stages of progress, and 1000 strong healthy plants, had been reduced to this condition, including different varieties of the fir, cedar, geranium, fuchsia, rose, jasmine and heath. The sight of this wholesale destruction, coupled with the fact that the whole were daily watered from one particular source, suggested the conclusion that the cause of the evil must reside in the water thus used; and this was accordingly examined. It yielded the following constituents, making in each imperial pint of 20 fluid ounces nearly $9\frac{1}{2}$ grains of solid matter entirely saline, without any organic admixture:—

Carbonate of lime	0·600
Sulphate of lime	0·462
Chloride of calcium	0·200
Chloride of magnesium	1·252
Chloride of sodium	6·906
	9·420

The mould around the plants and an infusion of the dead stems and leaves also afforded abundant evidence of the presence of much

chloride of sodium. Further inquiry showed that the well from which the water was procured had an accidental communication, by means of a drain, with the sea; and had thus become mixed with the salt water from that source, and had been used in this state for some weeks, probably from two to three months. From about that time the plants had been observed to droop; but it was not until nearly the whole of a valuable stock had been destroyed, that any extraordinary cause of the evil was suspected. To place it beyond doubt that the water was really the cause of the mischief, twelve healthy fuchsias were procured from a distance, and divided into two parts, half being watered morning and evening with the water in question, and the others with rain-water. In a week the six plants watered from the well had turned brown, and ultimately died, while all the rest remained perfectly flourishing. Assuming, from these facts, that the common salt in this water was the chief cause of the results described, it is proved that water containing about 7 grs. of salt in each pint is, in its continued use, an effectual poison to the weaker forms of vegetation; or that when a soil is continually watered with a weak solution of salt, it gradually accumulates in it until the soil becomes sufficiently contaminated to be unfit to support vegetable life. In either case an interesting subject of inquiry is suggested—What is the weakest solution of salt which can produce in any measure this poisonous effect? or, in other words, at what degree of dilution does the danger cease? For salt is an important natural constituent of much spring water, quite independent of any infiltration from the sea, as in this instance. Thus, the water of the artesian well, Trafalgar-square, London, contains in each gallon about 20 grs.; that at Combe and Delafield's brewery, 12·7; that at Wolverhampton Railway Station, 6; one lately sunk at Southampton, for supplying a private manufactory, 40. May it not be asked, whether the subject of the suitableness of waters in general for the various purposes to which they are applied, be it in manufactures or for steam-engines, domestic purposes or drinking, is not worthy of a greater share of scientific attention than it has hitherto commanded?

On the various Applications of Gutta Percha. By Mr. Whishaw.

The author, after observing that gutta percha was the concrete juice of a large tree of the same name, abounding in Borneo, &c., obtained by tapping the tree periodically by the Malays, stated that its introduction into this country was purely accidental, Dr. Montgomery having transmitted the first sample of it to the Society of Arts in 1843, at which time he (Mr. Whishaw) was secretary to that Society. The first articles of use made of gutta percha in this country were laid before the Society of Arts in 1844, and consisted of a lathe-band, a short length of pipe and a bottle-case, which he had himself made by hand, having caused the concrete substance to become sufficiently plastic by immersing it in hot water. He also produced casts from medals, which attracted considerable attention at the time, and surgical instruments were soon after made of this

new material. It was also adapted to commercial uses; and from the period mentioned to July 11th in the present year between 600 and 700 tons had been imported for the Gutta Percha Company. From 20 to 60 tons were now regularly imported every month. Contrary to the general opinion that gutta percha is a simple hydrocarbon, Mr. R. L. Cane found it in its ordinary state to consist of at least two distinct materials, besides a notable proportion of sulphur, viz.—1st, a white matter, gutta percha in its pure state; 2nd, a substance of a dark brown colour. Various experiments were made to ascertain its strength when mixed with other matters, and also as to what pigments would mix with it without rendering it brittle or deteriorating its qualities. From these it appeared that the only pigments that could altogether be relied on to be used with gutta percha were orange lead, rose pink, red lead, vermilion, Dutch pink, yellow ochre and orange chrome. Under the influence of heat and pressure, gutta percha would spread to a certain extent, and more so if mixed with foreign matters. All the mixtures composed of gutta percha and other substances which had been subjected to experiment, except that containing plumbago, were found to increase its power of conducting heat; but in its pure state gutta percha was an excellent non-conductor of electricity. The best composition for increasing the pliability of gutta percha was that formed in conjunction with caoutchouc tar, and next in order that of its own tar; and the best material at present known for moulding and embodying was obtained by mixing gutta percha with its own tar and lamp-black. In describing the process of manufacturing gutta percha, the author observed, that rude blocks of the material were first cut into slices, by means of a cutting machine formed of a circular iron plate of about 5 feet in diameter, in which there are three radical slots furnished with as many knives or blades. The blocks are placed in an inclined shoot, so as to present one end to the operation of the cutters. The slices are then placed in a wooden tank, containing hot water, in which they are left to soak until found in a plastic state. They are afterwards passed through a mincing cylinder, similar to that used in paper mills for the conversion of rags into pulp, and then thoroughly cleansed in cold-water tanks; the water, in cases of impure gutta percha, being mixed with a solution of common soda or chloride of lime. It is next put into a masticating machine, such as is used in the manufacture of caoutchouc, and then pressed through rollers; thus being converted into sheets of various width and thickness. When necessary, the sheets are again masticated, and again passed through rollers. These sheets are subsequently cut into boards by vertical knives, placed at the further end of the table, along which the sheets are carried by a cloth or web to another roller, round which they pass, and are cut into the required widths. The bands or straps are then removed, and coiled up ready for use. Driving bands for machinery are thus made, and shoe soles and heels are stamped out of similar sheets of gutta percha. In making tubes or pipes, either of gutta percha or any of its compounds, a mass of gutta percha, after being thoroughly masticated,

is placed in a metal cylinder furnished with a similar piston, by which it is pressed down into an air-box, kept hot with steam, which has at its lower end a number of perforations, through which the plastic material is forced into a cup, whence it passes out, round a core, into the desired tubular form, and thence through a gauge to the required size, and into a receiver of cold water, being drawn to the other end of a long trough by a cord passing round a pulley at the far end of the trough, and returning to the person in attendance on the machine, who gradually draws the pipe away from the air-machine. Thus tubes of considerable length and diameter are made to a very great extent, and are used for the conveyance of water and other liquids, and are now under test for the conveyance of gas.

On the Extraction of Silver from some of its Ores by the Wet Way. Dr. Percy.

This communication proposes to treat silver ores with hyposulphite of lime and chloride of lime; and from experiments detailed by Dr. Percy there appears every reason to believe that these substances may be employed œconomically, and both gold and silver extracted by an easy and effective method.

On the Colouring Matters of Madder. By Mr. J. Higgin.

The author, after describing the three colouring matters of madder, xanthine, rubiacine and alizarine, and the means he employs to separate them in a pure form, proceeds to show that the opinion usually entertained, that it is the alizarine only which is the valuable part of madder, is incorrect; and several experiments are adduced to prove that in proper circumstances, such as obtain in ordinary madder dyeing, the xanthine and rubiacine contribute very materially to the effect. They are shown not to act directly, but become changed into alizarine, which then combines with the mordants. This change is considered by the author to be induced by a peculiar azotized ferment found in madder, whereby xanthine becomes rubiacine and this latter alizarine; and the opinion is held out that all colouring matter in madder is derived primarily from xanthine.

Report on the Air and Water of Towns. By Dr. Smith.

In commencing his report, the author says it has long been believed that the air and the water have the most important influence on our own health; and superstitions have therefore constantly attached themselves to receptacles of the one and emanations of the other. The town has always been found to differ from the country; this general feeling is a more decisive experiment than any that can be made in a laboratory. The author proceeds to examine all the sources from which the air or the water can be contaminated. The various manufactures of large towns, the necessary conditions to which the inhabitants are subjected, and the deteriorating influences of man himself, are explained. If air be passed through water, a certain amount of the organic matter poured off from the lungs is to be detected in it. By continuing this experiment for three months,

Dr. Smith detected sulphuric acid, chlorine, and a substance resembling impure albumen. These substances are constantly being condensed upon cold bodies, and in a warm atmosphere the albuminous matter very soon putrifies and emits disagreeable odours. The changes which this substance undergoes by oxidation, &c. are next examined, and shown to give rise to carbonic acid, ammonia, sulphuretted hydrogen, and probably other gases. The ammonia generated fortunately from the same sources as the sulphuretted hydrogen materially modifies its influences. The consequences of the varying pressure of the atmosphere have been observed; and it is shown that the exhalations of sewers, &c. are poured out in abundance from every outlet when the barometric pressure is lowered. By collecting the moisture of a crowded room by means of cold glasses, and also dew in the open air, it was found that one was thick, oily, and smelling of perspiration, capable of decomposition and production of animalcules and confervæ, but the dew beautifully clear and limpid. Large quantities of rain-water have frequently been collected and examined by Dr. Smith; and he says, I am now satisfied that dust really comes down with the purest rain, and that it is simply coal ashes. No doubt this accounts for the quantity of sulphites and chlorides in the rain, and for the soot, which are the chief ingredients. The rain is also often alkaline, arising probably from the ammonia of the burnt coal, which is no doubt a valuable agent for neutralizing the sulphuric acid so often found. The rain-water of Manchester is about $2\frac{1}{4}°$ of hardness; harder, in fact, than the water from the neighbouring hills which the town intends to use. This can only arise from the ingredients obtained in the town atmosphere. But the most curious point is the fact that organic matter is never absent, although the rain be continued for whole days. The state of the air is closely connected with that of the water; what the air contains the water may absorb, what the water has dissolved or absorbed it may give out to the air. The enormous quantity of impure matter filtering from all parts of a large town into its many natural and artificial outlets, does at first view present us with a terrible picture of our underground sources of water. But when we examine the soil of a town, we do not find the state of matters to present that exaggerated character which we might suppose. The sand at the Chelsea Water-works contains only 1·43 per cent. of organic matter after being used for weeks. In 1827 Liebig found nitrates in twelve wells in Giessen, but none in wells two or three hundred yards from the town. Dr. Smith has examined thirty wells in Manchester, and he finds nitrates in them all. Many contained a surprising quantity, and were very nauseous. The examination of various wells in the metropolis showed the constant formation of nitric acid, and in many wells an enormous quantity was detected. It was discovered that all organic matter, in filtrating through the soil, was very rapidly oxidized. The presence of the nitrates in the London water prevents the formation of any vegetable matter; no vegetation can be detected, even by a microscope, after a long period. The Thames water has been examined from near its source

to the metropolis, and an increasing amount of impurity detected. In the summary to this report, Dr. Smith states that the pollution of air in crowded rooms is really owing to organic matter, and not merely carbonic acid; that all the water of great towns contains organic matter; that water purifies itself from organic matter in various ways, but particularly by converting it into nitrates; that water can never stand long with advantage unless on a large scale, and should be used when collected or as soon as filtered.

On a new Process for analysing Graphite, natural and artificial. *By* Prof. R. E. Rogers *and* Prof. W. B. Rogers.

The new process is founded on the fact, that a mixture of bichromate of potash and sulphuric acid, when applied in great excess to minutely divided graphite, converts the carbon rapidly and completely into carbonic acid. The fact of such a reaction was noticed by the authors more than two years ago; but the details of the present process were not matured until the winter of 1847, since when it has been used in a number of instances for determining the carbon of graphite, and always with consistent and satisfactory results.

On the Oxidation of the Diamond in the Liquid Way. *By* Prof. R. E. Rogers *and* Prof. W. B. Rogers.

The processes for oxidizing the diamond hitherto described consist in actually burning this gem, either in the air or in oxygen gas, or in some substance rich in oxygen, as nitrate of potash. In all these experiments a very elevated temperature is required. It is therefore interesting to discover that the diamond may be converted into carbonic acid in the liquid way and at a moderate heat by the reaction of a mixture of bichromate of potash and sulphuric acid—in other words, by the oxidating power of chromic acid. To succeed in this experiment, it is necessary to reduce the diamond to the most minute state of division. A single grain of the gem would suffice for many experiments. In repeated trials more than half a grain has never been used, and clear evidence of the oxidation has been obtained by the evolution of carbonic acid. The bichromate of potash when heated is always found to afford some carbonic acid; but error is avoided by first heating the acid alone in the retort to about 350°, then adding the bichromate by degrees, and stirring the mixture so as to effect a complete separation of chromic acid. A very brisk reaction takes place, much oxygen is disengaged, and with it any carbonic acid which the materials themselves are capable of evolving. When no more carbonic acid can be detected by lime-water tests, the powdered diamond is carefully added. The evolution of carbonic acid is soon evinced by the growing milkiness of lime-water, and this continues slowly to increase as long as there is any free chromic acid in the retort. The chief point of interest in the subject, however, is the fact, now published for the first time, that the diamond is capable of being oxidated in the liquid way and at a comparatively moderate temperature, varying between 350° and 450°.

THE CHEMICAL GAZETTE.

No. CXLII.—September 15, 1848.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a new Product of the dry Distillation of Wood.

By Dr. E. Schweitzer.

In the course of an examination of the constituents of *crude pyroxylic spirit,* I have discovered a substance which has hitherto not been observed, as far as I am aware, and which stands in a very interesting relation to pyroxanthine (eblanine), discovered by Scanlan, and more minutely examined by Gregory and Apjohn. Before communicating the results at which I have arrived, it will be necessary to notice the statements of these chemists in reference to pyroxanthine.

According to Gregory, pyroxanthine is originally contained in the crude pyroxylic spirit, and is prepared from it in the following manner:—About 15 per cent. is distilled from the crude spirit. The brownish-yellow acid distillate is mixed with hydrate of lime, which neutralizes the acetic acid present, and precipitates the colouring substance. When the whole is now submitted to a fresh distillation, the wood-spirit passes over colourless, while a dark-coloured residue remains, consisting of acetate of lime and pyroxanthine. This latter is treated with dilute muriatic acid, which removes the lime and the acetic acid; the residue is frequently exhausted with small quantities of alcohol, which at first removes the resinous substance, imparting the brown colour; subsequently the alcohol is coloured more and more of a pure yellow by the pyroxanthine, which separates in crystals on cooling, and may be obtained perfectly pure by recrystallization from alcohol. Pyroxanthine crystallizes in needles of the colour of the nitropicrate of potash; it dissolves in alcohol, æther and acetic acid on the application of heat, but is insoluble in water, caustic potash and ammonia; in the open air it begins to sublime at about 273°, but in a confined space it cannot be volatilized without decomposition. This behaviour is in contradiction to the fact, that the pyroxanthine is contained in the most volatile portion of the products of distillation, viz. in the pyroxylic spirit. Gregory explains this by assuming that pyroxanthine is highly volatile in the vapour of pyroxylic spirit.

The crude pyroxylic spirit which I employed for my investigation was that which passes over first in the distillation of the crude pyroligneous acid. In the manufactory it had not been submitted to

any further purification, as for instance the usual rectification over lime, and consequently constituted the original products of dry distillation. I submitted more than 200 lbs. of this liquid to a fractioned distillation on the water-bath; as soon as what passed over was scarcely combustible, that which followed was collected separately, and the distillation continued until merely water mixed with a little acetic acid passed over. The residue was an acid aqueous liquid, and a pitchy mass adhering to the sides of the still.

My attention was first drawn to the second aqueous portion of the distillate; it was of a very faint brownish-yellow colour, and possessed the peculiar empyreumatic odour of the crude pyroxylic spirit in a high degree, and an excessively acrid and burning taste. On supersaturating a sample with potash, a chrome-yellow precipitate formed in a few seconds, which led me to suspect a separation of pyroxanthine. To decide this, I immediately treated a considerable quantity of the liquid with potash. At first a considerable orange-coloured flocculent precipitate was formed, and subsequently a reddish-yellow resinous mass separated; the first was collected upon a filter, washed with water, and then treated repeatedly with small quantities of hot alcohol. The first alcoholic solutions were of a dark red colour, and left a resin upon evaporation; subsequently the alcohol acquired an intense yellow colour. The whole of the residue was now dissolved in boiling alcohol, from which on cooling a large quantity of pyroxanthine crystallized. After frequent recrystallization, to remove the small traces of adherent resin, I obtained it perfectly pure, with all the properties assigned to it by Gregory.

With respect to the preparation of pyroxanthine, I have still to observe, that in order to obtain a pure product, it is essentially requisite to extract the greater portion of the resin first, by treating the mixture successively with small quantities of boiling alcohol, although a large amount of pyroxanthine is thus lost. If the mixture is dissolved at the outset in a sufficient quantity of boiling alcohol, the greater portion of the pyroxanthine crystallizes, it is true, on cooling; but the crystals are of a dirty brownish-yellow colour, and cannot be obtained of a pure yellow colour even by frequent recrystallization.

As very dilute solutions of pyroxanthine are of an intense yellow colour, while the liquid from which I prepared it was nearly colourless; since, moreover, the separation of the pyroxanthine did not occur simultaneously with the neutralization of the acetic acid by potash, I was led to suspect that the pyroxanthine is not contained as such in solution in the acid liquid, but had been produced by the action of the potash upon some still unknown compound. After several unsuccessful experiments, I at last succeeded in isolating the latter in the following manner:—I added æther to the liquid in question till no more was dissolved, and a pretty considerable layer formed on the surface, and set the whole aside for about twenty-four hours, frequently agitating it. The ætherial layer was then separated from the subjacent liquid and submitted to distillation in the water-bath; as soon as no more æther passed over, a liquid

residue remained, which on being mixed with water separated as a *heavy* brownish-coloured oil. A sample of it dissolved in dilute spirit and treated with potash, afforded a copious yellow precipitate containing pyroxanthine.

A considerable quantity of this oily body was also procured from the spirituous liquid obtained in the first distillation of the crude pyroxylic spirit, by submitting it to repeated distillation, and treating the aqueous liquid which each time remained in the still with æther.

To obtain the substance pure, it was first washed several times with water, and then distilled with water on the sand-bath. The distillation is greatly impeded by the violent succussion. I observed, however, that when in distillations of this kind glass tubes are placed in the retort, the thumping can be almost entirely prevented, the heavier hot liquid ascending in the tubes and flowing over upon the upper and colder liquid. A dark brown resin, still mixed with a little oil, remained in the retort; the yellow-coloured product was again submitted to distillation with water; the first portions were nearly colourless, while those which followed became more and more yellow, and the residue in the retort acquired a dark colour in proportion.

The oil purified by distillation with water possesses the following properties:—It is heavier than water, possesses a disagreeable odour, calling to mind smoked fish, and a strong biting taste. It dissolves entirely, but with difficulty, in water, more easily however in hot than in cold; so that from a hot saturated solution a portion of the oil again separates on cooling. It is very readily soluble in æther, alcohol and pyroxylic spirit. It is not very volatile; it cannot be distilled alone without experiencing a considerable decomposition. The contents of the retort are quickly coloured dark yellow, and at last black, with the production of a large amount of resin; gradually the distillate acquires a dark colour, but still retains in other respects its former properties.

As above stated, it can be obtained colourless on slow distillation with water, but it soon reacquires a yellowish colour, especially under the influence of light and air; this colour increases with time: at 18° F. the greater portion becomes solid, in which state it forms a white fatty mass.

When an aqueous or alcoholic solution is mixed with potash, the formation of pyroxanthine takes place; this is likewise produced by baryta and lime, and even by the carbonated alkalies with the assistance of heat: ammonia effects the decomposition in the cold only after several hours, but in a few minutes at a boiling temperature. An alcoholic solution of the oil yields no precipitate with acetate of lead; but on the addition of ammonia, a large white flocculent precipitate is formed. Protosalts of mercury are quickly reduced by the oil and heat.

To ascertain what other products besides pyroxanthine are formed on the decomposition of the new substance by alkalies, a considerable quantity of the former was dissolved in water, the solution mixed with an excess of pure caustic potash, the abundant yellow

precipitate, as soon as it had subsided, collected on a filter, and the filtered alkaline liquid immediately saturated with sulphuric acid. This separates a very small quantity of a soft resin, which distinctly possesses the odour of *creosote*. The liquid separated from it was now shaken with an excess of æther, and the æther subsequently submitted to distillation on the water-bath, when it left behind a yellowish oil, which was purified by distillation with water. With respect to its physical properties, it exhibited little difference from the original substance, possessed a similar odour, was heavier than water, and somewhat soluble in it, &c. Its aqueous or alcoholic solution however produced with potash not a trace of pyroxanthine. It dissolves with great difficulty in potash, and only with the assistance of heat. When boiled for some time with potash, it is completely decomposed.

On saturating the boiled dark solution with an acid, an oily substance again separated, which could be separated by distillation with water into a resin and a volatile oil, possessing in a remarkable degree the characteristic odour of *creosote*, and also the other physical properties of the latter. This decomposition however requires more accurate investigation before any positive conclusion can be drawn in reference to the production of creosote. From the aqueous liquid, which had been shaken with æther, the æther held in solution was in the first place removed by distillation in the water-bath, upon which it was supersaturated with sulphuric acid, and the greater portion distilled off on the sand-bath. The clear, colourless, acid distillate was mixed with carbonate of soda until it exhibited an alkaline reaction; it was then evaporated to dryness on the water-bath, and the residuary saline mass again distilled with sulphuric acid. I now obtained a strongly *acid liquid*, of a disagreeable odour, exactly resembling butyric acid. It has the property of instantly reducing protosalts of mercury even in the cold, by which it is distinguished from the butyric, acetic and formic acids. I prepared this acid several times, varying the mode of preparation; and it always possessed the property of reducing protosalts of mercury in the same degree. In other respects it has some resemblance to acetic acid, and is perhaps a conjugate combination of the latter with some other organic substance.

A considerable amount of *resin* separates with the pyroxanthine. By exhausting the mixture with alcohol of about 0·876 spec. grav., evaporating the solution, again treating the residue with alcohol, and repeating these operations several times, it may be obtained nearly pure from pyroxanthine. It is of a reddish-brown colour, readily fusible, insoluble in water, but soluble in alcohol and æther. It dissolves with difficulty in potash, especially in the cold. Its alcoholic solution is only precipitated by a solution of basic acetate of lead in alcohol on the addition of ammonia.

The results of the experiments above communicated may be briefly stated as follows:—

1. A peculiar, heavy, empyreumatic oil is contained in large quantity in crude pyroligneous spirit.

2. This however is probably a mixture of two distinct substances, of which one becomes solid at 18°, whilst the other remains liquid at this temperature.

3. Pyroxanthine is not contained as such in the crude pyroligneous spirit, but is first produced by the action of alkalies and alkaline earths upon the empyreumatic oil, or rather one of its constituents (pyroxanthogen).

4. On the decomposition of the pyroxanthogen by potash, there is simultaneously formed with the pyroxanthine a neutral resin and a volatile acid which very readily reduces protosalts of mercury.

I hope soon to be able to communicate a more accurate analytical investigation of this subject.—*Journ. für Prakt. Chem.*, July 15, 1848.

Notice respecting Amiduline. By Prof. F. Schulze.

I have applied the above name to a modification of starch which forms the transition between true starch and inuline or dextrine; it is an intermediate stage, which precedes all the metamorphoses of starch into dextrine, and is characterized by being readily and entirely soluble in hot water. It again separates from the concentrated aqueous solution after a longer or shorter time, owing to its insolubility in cold water; it reacts with iodine like starch.

This compound calls to mind Jacquelin's amylum granules, with which it is perhaps identical. It is distinguished from inuline by its reaction with iodine, and by not being converted into sugar on boiling its aqueous solution. It resembles dextrine in its solution, deviating the plane of polarization considerably to the right. It exhibits no reaction with lime and barytic water, nor with basic acetate of lead, and differs consequently in this respect from the so-called solution of starch.

With respect to the preparation of this substance, the same method is followed as for dextrine, only with this difference, that the boiling of the mixture of sulphuric acid, water and starch is discontinued as soon as the starch is dissolved. The acid is neutralized with carbonate of lime while the liquid is still hot. After the lapse of some time, frequently of several days, the amiduline separates in flakes easy of filtration, and which on drying assume all the appearance of white sago. Its elementary composition agrees exactly with that of starch.—*Journ. für Prakt. Chem.*, xliv. p. 178.

On Osman-osmic Acid and its Salts. By J. Fritsche *and* H. Struve.

The authors discovered this acid in attempting to prepare Fremy's osmiamide, by the addition of chloride of ammonium to a solution of osmic acid in caustic potash. The potash salt of the acid is most easily obtained by directly adding caustic ammonia to the solution of osmic acid and caustic potash. The liquid quickly acquires a pale yellow colour, and the newly-formed salt either separates imme-

diately as a crystalline powder, or is obtained by evaporation at a gentle heat. The potash is not requisite for the formation of the acid, but it must be added, as the preparation of the far more easily soluble salt of ammonia from the crude solution is not so readily done. On the addition of ammonia to osmic acid, 1 equiv. of ammonia parts with the whole of its hydrogen, and 1 equiv. osmic acid with the whole of its oxygen, the osmium and nitrogen combining, and uniting at the same time with 1 equiv. undecomposed osmic acid. What becomes of the fourth equivalent of oxygen could not be determined. The authors consider the new compound as a combination of the nitruret of osmium with osmic acid, $OsN + OsO^4$; it is the first example of an acid with a nitruret as a conjunct. This conjunct might, for all similar acids, be designated by the termination *an* appended to the abbreviated name of the metal as the authors have done in the present instance. The salts of the acid are remarkable from their being decomposed by heat with explosion, probably owing to the nitruret of osmium; the products of the decomposition are osmium and osmic acid. The protosalt of mercury is volatilized when rapidly heated without any explosion, giving off a strong odour of osmic acid. The salts are crystalline, and dissolve more or less readily in water. The free acid may be obtained by decomposing the baryta salt with sulphuric acid, or the silver salt with hydrochloric acid; it forms a yellow solution, which is not very stable, and cannot be concentrated without disengaging a gas and yielding a brown precipitate. The acid decomposes carbonates with effervescence. Zinc dissolves in it with a slight disengagement of gas; but the acid soon decomposes, and deposits a blackish-brown body.

When the salts are calcined with a mixture of hydrate of potash and carbonized sugar, they do not afford ammonia, the nitruret of osmium being probably destroyed at a temperature lower than that required by the carbon to decompose the water of the hydrate; on this account the nitrogen was determined in the state of gas.

The Potash Salt, $KO, OsO^4 + OsN$, is obtained by adding osmic acid to a hot mixture of hydrate of potash and ammonia, or by pouring ammonia into a hot solution of osmate of potash with excess of base. If the solution is sufficiently concentrated, the salt is deposited on cooling in yellow granules; otherwise it must be evaporated at a gentle heat. To obtain larger crystals, a cold saturated solution is left to spontaneous evaporation, when crystals are obtained more than a line in length, which are elongated cubic octahedrons. They contain no water of crystallization. This salt is not decomposed at 356° F., but at a higher temperature it acquires a darker colour and explodes. It is not very soluble in water, and still less so in alcohol, without however being decomposed; it is insoluble in æther. It furnished on analysis—

Potash	16·126	1 =	16·137
Osmium	67·900	2	68·105
Nitrogen	4·820	2	4·797
Oxygen.....	11·154	4	10·961

The Soda Salt may be prepared in the same manner as the salt of potash; but the best plan is to triturate the silver salt with chloride of sodium until the yellow colour has become almost completely changed into white, upon which it is filtered and evaporated over sulphuric acid. The solution first acquires a syrupy consistence, and then crystallizes in large prisms containing water of crystallization, in which they melt with a gentle heat, and which they subsequently lose without the salt being decomposed. The salt is very soluble in water, and likewise more soluble in alcohol than the salt of potash.

The Ammonia Salt is decomposed too quickly when prepared directly with osmic acid and ammonia. It is better to triturate the silver salt in water with chloride of ammonium, and to evaporate the filtered solution over sulphuric acid. In this manner large anhydrous crystals are obtained, which are isomorphous with the salt of potash, detonate at 357°, and are very soluble in water and in alcohol; æther does not precipitate the salt from the alcoholic solution, which may moreover be boiled without any decomposition resulting.

The Baryta Salt is most easily obtained by decomposing the silver salt with chloride of barium; it crystallizes in brilliant yellow needles several lines in length, which detonate at 302°, and are very soluble in water. This salt has the following composition:—

Baryta	23·880	1 =	23·789
Osmium	61·070	2	61·890
Nitrogen	4·269	2	4·360
Oxygen.....	10·836	4	9·961

The Zinc Salt is very soluble, and could not be obtained in the solid state. It combines with 2 equivs. of ammonia, forming an insoluble salt. It is this compound which is precipitated when osmic acid is poured into a solution of oxide of zinc in ammonia; it forms a pale yellowish powder, which subsides very quickly, and may be dried in the air after having been washed with ammonia. It does not dissolve in water, but is decomposed by it, especially when boiled; one of the equivalents of ammonia and the oxide of zinc are separated, and the liquid contains osman-osmate of ammonia. The salt detonates at 302°.

The Lead Salt is not precipitated on mixing a solution of the potash salt with nitrate of lead; but after some time crystals separate, which however easily alter. The nitrate of lead, on the contrary, produces in the solution of the soda or ammonia salt a yellow crystalline precipitate, which becomes brown at the surface during the washing, and which appears to contain 2 atoms of oxide of lead to 1 atom of acid.

The acetate of lead produces a dirty yellow amorphous precipitate in a solution of the potash salt, which however soon parts with osmic acid and turns reddish-purple. Acids dissolve this red salt, and ammonia appears to precipitate it from this solution unaltered.

A solution of chloride of lead produces in a solution of the soda or ammonia salt a yellow crystalline precipitate, the com-

position of which is represented by the formula $PbCl + PbO, OsO^4 + OsN$.

The Protosalt of Mercury is a yellow crystalline precipitate, which is obtained by double decomposition, is insoluble in water, soluble in nitric acid, and is decomposed by chlorides like the silver salt. It does not detonate, but sublimes slowly even when quickly heated, and gives off a strong odour of osmic acid.

The Persalt of Mercury is obtained by triturating the silver salt with chloride of mercury and water; it is deposited in prismatic crystals from the filtered solution; nevertheless the solution and the crystals soon turn black.

When the potash salt is mixed with a solution of chloride of mercury and ammonia is added, a crystalline precipitate is formed, which appears to be a combination of the salt of mercury with ammonia; but it has likewise little stability, and quickly turns black and is destroyed.

The Silver Salt is prepared by dissolving osmic acid in an ammoniacal solution of a silver salt, and saturating the ammonia in excess with a slight excess of nitric acid, or more simply by precipitating the potash salt with nitrate of silver. It constitutes a yellow crystalline powder, which may be dried *in vacuo* over sulphuric acid and in the dark. It blackens when exposed to the light, and even in darkness, after some length of time diffusing the odour of osmic acid. It detonates violently at 176°, under the hammer, and also when sulphuretted hydrogen is passed over the dry salt. It is sparingly soluble in water and in nitric acid, but dissolves readily in ammonia. On submitting this solution to spontaneous evaporation, a combination of this salt with ammonia is obtained. Nitric acid decomposes it with the assistance of heat; the acid at first becomes brown, and then colourless, giving off osmic acid.—Berzelius's *Jahresbericht* for 1848, p. 92.

On the Lactate of Bismuth. *By* H. Engelhardt.

Carbonate of bismuth and the hydrated oxide of bismuth are very sparingly soluble in lactic acid; nevertheless no insoluble lactate is formed. If, after treating the acid with the carbonate of bismuth or the hydrate, it is evaporated to a syrupy consistence, a salt crystallizes from it in microscopic needles on cooling. This salt is purified from adherent lactic acid by treating it first with alcohol and then with æther. However, this method cannot be recommended for the preparation of the salt; it was therefore attempted to procure it by the decomposition of lactate of baryta with sulphate of bismuth; but no lactate of bismuth was obtained, the decomposition proceeding very slowly, owing to the sulphate of baryta coating the insoluble sulphate of bismuth; for it was evident, in a subsequent examination of the salt $2BiO^3 + C^{12} H^{10} O^{10}$, which is produced under these circumstances, that it is entirely insoluble in water. It would therefore have been impossible to have extracted it from the paste of sulphate of baryta.

The preparation of the lactate of bismuth succeeded best by mixing a concentrated solution of lactate of soda with a saturated solution of oxide of bismuth in nitric acid. A large excess of the first salt should be avoided, as it prevents the crystallization of the lactate. When both the solutions are very concentrated, a crystalline paste separates, consisting of nitrate of soda and lactate of bismuth. To separate the lactate, the mixture is dissolved in as little water as possible, when a turbidness is produced only when nitrate of bismuth is mixed with the salts, for the lactate of bismuth dissolves with the nitrate of soda without any milkiness, and, when set aside, soon separates from the concentrated solution in crystalline crusts. So much alcohol is added to the mother-ley as to render it turbid, upon which the vessel is covered and set aside; in a few days a second crop of crystals separates, which have the same composition as the former. More salt may be obtained by the repeated addition of alcohol; larger quantities of alcohol precipitate nitrate of soda at the same time, which can then only be separated with loss from the lactate by water. The analysis of a salt perfectly free from nitric acid, which experienced no loss on being exposed to 212°, led to the formula $BiO^3, C^{12} H^{10} O^{10} = 2BiO^3, 3C^{12} H^{10} O^{10} + BiO^3$:—

Carbon	17·933	..	12	18·036
Hydrogen	2·553	..	10	2·505
Oxygen	..	..	10	20·040
Oxide of bismuth	59·194	59·099	1	59·419

This salt, $BiO^3, C^{12} H^{10} O^{10}$, dissolves very sparingly in cold water, but to a considerable extent when boiled. The solution however does not crystallize on cooling, but after evaporation deposits some crystalline crusts, which are dissolved by a little water; but the solution is rendered very turbid by more water. The author has not examined this reaction more closely, but it would appear that the salt is converted on boiling into an acid salt, which is again decomposed by a large amount of water, and converted into the compound $2BiO^3, C^{12} H^{10} O^{10}$, for the residue insoluble in boiling water presents all the characters of that compound.

The salt mentioned at the commencement of this paper, which is produced on treating carbonate of bismuth or the hydrated oxide with an excess of lactic acid, has the same composition; it left 59·155 per cent. of oxide of bismuth.

A lactate of bismuth of a different composition, with the formula

$$2BiO^3, C^{12} H^{10} O^{10} = 2BiO^3, 3C^{12} H^{10} O^{10} + 4BiO^3,$$

was obtained by dropping nitrate of bismuth into a moderately-dilute solution of lactate of soda, so that the latter salt was always present in excess. After long boiling, a considerable pulverulent precipitate fell, which was freed from nitric acid by washing with water, and dried at 212°, when it experienced no loss; it left behind 74·329 per cent. oxide of bismuth. This salt is insoluble in cold and boiling water, and is likewise not decomposed by water; for such a precipitate, which had been exhausted by boiling water, left 73·92 per cent.

oxide of bismuth. On treating basic nitrate of bismuth with lactate of soda, a very imperfect decomposition resulted.—Liebig's *Annalen*, lxv. p. 367.

On the Action of Acids upon Amygdaline. By Prof. Wöhler.

The composition of amygdaline is expressed by the formula $C^{40} H^{27} NO^{22}$. There is very little doubt that it is one of the so-called conjugate compounds. From the circumstance that it is separated by the influence of emulsine into sugar, prussic acid and oil of bitter almonds, it might be suspected that it really contains these substances as proximate constituents, for—

1 equiv. oil of bitter almonds	$C^{14} H^{6} O^{2}$
1 equiv. prussic acid.....	$C^{2} H N$
2 equivs. sugar	$C^{24} H^{20} O^{20}$
give 1 equiv. amygdaline	$C^{40} H^{27} N O^{22}$

But it might also be regarded as a combination of the protocyanide of benzoyle, $C^{14} H^{5} + C^{2} N$, with 2 atoms of gum :—

1 equiv. benzoyle	$C^{14} H^{5}$
1 equiv. cyanogen.....	$C^{2} N$
2 equivs. gum	$C^{24} H^{22} O^{22}$
	$C^{40} H^{27} N O^{22}$

On its metamorphosis, the elements of 2 atoms of water would separate from the gum and pass to the protocyanide of benzoyle, when the gum would appear as sugar, and the cyanide of benzoyle in the form of prussic acid and oil of bitter almonds.

The action of acids upon amygdaline agrees perfectly well with both views; it is converted by them into formobenzoilic acid and a humus-like substance, while the whole of the nitrogen is separated in the form of an ammonium salt; the same decomposition consequently takes place as prussic acid and sugar or gum experience by acids. Sugar or gum yields the humus-like substance, and the formic acid produced from the prussic acid combines with oil of bitter almonds to form formobenzoilic acid. I have examined this reaction, it is true, only with muriatic acid; but undoubtedly all the stronger acids would act in a similar manner.

A solution of amygdaline in fuming muriatic acid soon acquires on heating a yellow, and then a brown colour, and on the further application of heat, a large quantity of a blackish-brown, pulverulent, humus-like substance separates. On filtering the humine, and evaporating the brown liquid in the water-bath, a blackish-brown syrupy mass remains, which is a mixture of humic acid, chloride of ammonium and formobenzoilic acid. The latter can be extracted with æther, and obtained in large tabular rhombohedrons. Its solution immediately disengaged carbonic acid and oil of bitter almonds when heated with manganese; moreover, the analysis of the acid and of its crystalline silver salt proved it to be formobenzoilic acid. On evaporating the acid liquid at a higher temperature than 212°, a portion of the

formobenzoilic acid experiences an alteration, which deserves further examination. It becomes amorphous, forms a solution with a small quantity of water, but is precipitated, on the addition of more water, as a heavy yellowish oil without odour. The same change was observed with formobenzoilic acid prepared from bitter almond water. A quantity of crystallized chloride of ammonium was obtained from the mass which had been exhausted with æther.

In the hope of producing directly from amygdaline the æther of formobenzoilic acid, which is still unknown, muriatic acid gas was passed into a mixture of alcohol and amygdaline. In proportion as the mass became saturated with it and heated, the amygdaline gradually dissolved to a clear solution, and nothing separated on cooling. The gum products were not formed in this case, and the liquid acquired but a very faint brownish tint. After some days a powder separated, which proved to be chloride of ammonium, more of which separated on the addition of æther. On the addition of a large quantity of æther, an aqueous acid liquid separated, which contained the chloride of ammonium, but no sugar. After it had been repeatedly shaken with æther, the ætherial solution was removed, and the æther distilled off. It left a brown syrup, which on mixture with water sank as a heavy liquid to the bottom. I have not examined this substance more minutely, but it may be considered with great probability to be the æther of amygdalic acid, produced by the sugar or gum in the amygdaline not being converted into humine, but entering into combination with the generated formobenzoilic acid; for the composition of amygdalic acid, $HO + C^{40} H^{26} O^{24}$, is such that it may be looked upon as a combination of—

1 equiv. oil of bitter almonds	$C^{14} H^{6} O^{2}$
1 equiv. formic acid	$C^{2} H O^{3}$
2 equivs. sugar	$C^{24} H^{20} O^{20}$

Amygdalic æther is undoubtedly colourless in the unaltered state. Obtained in the above manner, it is light brown, heavier than water, not miscible with it, but soluble in it to a considerable extent, especially on the application of heat, when however it is decomposed. It has a bitter, somewhat astringent taste, and is but slightly or not at all volatile.—Liebig's *Annalen*, May 1848.

On the Preparation of some Combinations of Chromium. *By* Dr. M. Traube.

Chromic Acid.—We possess two processes for the preparation of this acid from chromate of potash and sulphuric acid, the one proposed by Fritzsche, the other by Warington. The evil of the first method is a great loss of chromic acid, which is not precipitated by the sulphuric acid; and the small flakes of precipitated chromic acid are not so easily separated mechanically from the sulphuric acid as the larger crystals. The evil of the second method is that too much sulphuric acid is used.

From the experiments which I made to ascertain what proportion

of the requisite materials was best suited for the preparation of chromic acid, I found that—

1. The bichromate of potash is not decomposed in the cold by twice the amount of sulphuric acid more than requisite to saturate the potash.

2. The bichromate of potash is decomposed when heated with nearly an equal weight of sulphuric acid when only half a part of water is present, but that unaltered bichromate of potash separates on cooling when 2 parts of water are present.

3. At least $9\frac{1}{2}$–$12\frac{1}{2}$ parts of concentrated sulphuric acid must be added to 1 part of bichromate of potash, dissolved respectively in $4\frac{1}{2}$ or $5\frac{1}{2}$ parts of water, to obtain chromic acid which shall not be contaminated with crystals of bisulphate of potash. Any further addition of sulphuric acid merely contributes to the production of more beautiful crystals. On employing still more sulphuric acid than Warington's method requires, I once obtained needles from 2 to $2\frac{1}{4}$ inches in length and $\frac{1}{3}$ a line in breadth.

The most advantageous method of preparing chromic acid is the following:—

1 part of bichromate of potash is heated with $3\frac{1}{2}$ parts of sulphuric acid and $2\frac{1}{2}$ parts of water; on cooling, the greater portion of the potash separates in the form of bisulphate. The liquid is decanted from these crystals, and mixed with 4 parts of sulphuric acid, which precipitates chromic acid in red flakes. It is heated, water added gradually until the whole is dissolved, and then evaporated till a crystalline film makes its appearance; on cooling, the chromic acid crystallizes. The supernatant sulphuric acid can be used to decompose fresh portions of the bichromate of potash.

The chromic acid thus obtained, after being dried upon a porous tile, may be purified in two ways:—

1. By cautious fusion in the air-bath. The admixture of chromate of potash and sulphuric acid is thus converted into insoluble sulphate of the oxide of chromium and potash, and insoluble sulphate of the oxide of chromium. When cold, the mass is left for some time in contact with water, and the solution of chromic acid decanted from the sediment and evaporated.

2. The crude chromic acid is dissolved in water, and sulphuric acid gradually added until chromic acid begins to be precipitated; the mixture is then evaporated to the appearance of a crystalline film, and set aside. The greater the quantity of solvent used, the more beautiful are the crystals which are obtained; they are dried upon a porous tile, and recrystallized from water. Chromic acid cannot be freed so readily and without great loss from chromate of potash by mere recrystallization from water, owing to its great solubility.

Blue Sulphate of the Oxide of Chromium.—1 part chromic acid, recrystallized from sulphuric acid, is dissolved in $1\frac{1}{2}$ part concentrated sulphuric acid. Alcohol is allowed to flow gradually in drops, from a funnel stopped with paper, to this mixture, which is surrounded by cold water. When the reduction is complete, absolute

alcohol is added, which immediately precipitates blue sulphate of chromium, which is washed with spirit. If too great an evolution of heat has occurred by the careless addition of the alcohol, and the salt has passed into the green modification, the solution is boiled with nitric acid, which, as found by Löwel, rapidly converts the green into the violet sulphate; the solution is then precipitated by alcohol. The blue sulphate of the oxide of chromium can be boiled with alcohol, the point of ebullition of which is 176°, without passing into the green modification.

Another method of preparing the blue sulphate of the oxide of chromium is the following:—1 part chromic acid is dissolved in $1\frac{1}{2}$ part concentrated sulphuric acid and $2\frac{1}{4}$ parts water, and a porcelain crucible filled with æther placed in the shallow dish containing the mixture. In the course of a few hours nearly the whole mass separates in minute crystals of the blue sulphate. The reduction is completed by a few drops of alcohol.

Chrome Alum.—1 part bichromate of potash is dissolved in 2 parts sulphuric acid and so much water at a gentle heat that the mixture does not deposit any crystals at the ordinary temperature. To avoid the evolution of too much heat, this solution is gradually poured into alcohol contained in a dish surrounded with cold water. A large portion of the chrome-alum immediately falls as a crystalline powder. The mother-ley is evaporated in the water-bath, after the addition of one-seventh part by weight of nitric acid to prevent the transition into the green modification, to nearly one-fourth of the original weight (the nitric acid included); an equal weight of alcohol is then added to the residue, and the mixture set aside; in the course of a night the greater portion of the chrome-alum contained in the mother-ley crystallizes. The crystals are dissolved in a flask at a temperature of 122° with constant agitation, and set aside to crystallize.—Liebig's *Annalen*, May, p. 165.

On the Preparation, Properties and Composition of the Polythionic Acids and their Salts. By F. Kessner.

Under the name of polythionic acids the author comprises the trithionic, tetrathionic and pentathionic acids, which he has submitted to a very complete investigation. It will be remembered that the compounds S^5O^7 and S^6O^7, assumed by Plessy to be distinct oxides, have been shown by Fordos and Gelis not to exist, and that Plessy was led by an error to admit them.

I. *Preparation of Trithionic Acid and its Salts.*

Trithionic Acid is obtained dissolved in water when the solution of the trithionate of potash is decomposed with the fluosilicate of potash. It is extremely unstable, and it was found impossible to concentrate the acid without decomposition into sulphurous and sulphuric acid, even at a temperature below 32° F.

The *Trithionate of Potash* is easily obtained, either according to Plessy's method by passing sulphurous acid into a solution of dithi-

onite of potash, or according to Langlois into one of sulphuret of potassium; in the latter case dithionite of potash is first formed, and from this the trithionate.

Trithionate of Soda.—The author attempted in vain to prepare this salt according to the directions of Plessy and Langlois. The author dissolved trithionate of potash and tartrate of soda in as little water as possible, and cooled this solution quickly to 32°. The liquid separated from the bitartrate of potash was evaporated *in vacuo* at a low temperature over sulphuric acid. When it had been concentrated to within one-half its bulk, sulphurous acid was given off. Sulphate and dithionite of soda were obtained, and no other product—decidedly no free sulphur. The decomposition must consequently have resulted according to the following equation—

$$3(NaO, S^3 O^5) = 4SO^2 + NaO, SO^3 + 2(NaO, S^2 O^2).$$

Trithionate of Baryta is obtained in brilliant laminæ when the aqueous solution of trithionic acid is saturated with carbonate of baryta and the solution mixed with a large excess of absolute alcohol. The solution of the salt in water is very soon decomposed, depositing sulphate of baryta. The air-dried salt gave on analysis—

Baryta	41·87	1	41·96
Sulphur.....	26·22	3	26·28
Oxygen.....	..	5	21·90
Water	..	2	9·86

Baumann has stated that trithionates are obtained by digesting dithionates with sulphur. These salts are obtained, according to him, very quickly when sulphurous acid is passed into a solution of alkaline sulphuret in which peroxide of manganese is suspended. According to him, the peroxide of manganese first becomes converted into the dithionate of the protoxide of manganese, which is then decomposed by the sulphuret of potassium into sulphuret of manganese, dithionate of potash and sulphur, when the two last substances combine in the nascent state, and produce trithionate of potash. Since however Langlois has shown that trithionate of potash can be very easily prepared from sulphurous acid and sulphuret of potassium, the author considers the peroxide of manganese in Baumann's experiment to be wholly indifferent, and that consequently no intermediate production of dithionate of potash can have taken place. Baumann, in making his experiment of digesting sulphur with dithionates, did not employ pure salts, but such as still contained free carbonated or caustic alkali; so that fallacy might easily have arisen from the action of the alkali upon the sulphur; moreover, this excess of alkali could not contribute to the production of trithionic acid, as the trithionate of potash is, on the contrary, converted by an excess of alkali into dithionite. According to the author's experiments, not a trace of trithionic acid is formed in this way; for on digesting solutions of pure and previously-crystallized dithionates of potash, soda and baryta with finely-divided sulphur (milk of sulphur), at different temperatures from 86° up to 212°, not a trace of trithionic acid could in any case be detected by salts of silver and cyanide of

mercury, nor one of its products of decomposition,—sulphurous and sulphuric acids.

II. *Preparation of Tetrathionic Acid and its Salts.*

The author has discovered an easier method of preparing the tetrathionic acid than those hitherto followed. Fordos and Gelis first obtained tetrathionic acid by treating dithionite of baryta with iodine, and removing the iodide of barium produced by alcohol. According to the author, this process is not advantageous, for the residue left by the alcohol dissolves in water with the separation of considerable quantities of sulphur and sulphate of baryta, and the solution then contains some trithionate of baryta, as first shown by Plessy. It was likewise shown by Plessy that tetrathionic acid is more permanent in the free state than in the presence of strong bases (the reverse of dithionous acid), when it very readily passes into trithionates with elimination of sulphur.

The author turns this behaviour to account in preparing tetrathionic acid, the stability of which in the isolated state is but slightly interfered with by the presence of weak bases. The starting-point is the dithionite of lead, the conversion of which into tetrathionate has already been described by Fordos and Gelis, but no further attention was paid to it. Dithionite of lead is prepared in the first place by dissolving 2 parts of hyposulphite of soda in hot water, and pouring this solution into an equally hot dilute solution of 3 parts of acetate of lead. The precipitate is washed with a large quantity of warm water, and mixed still moist with 1 part of iodine, and the mass frequently stirred; in the course of a few days the whole is converted into iodide of lead and a solution of tetrathionate of lead, which is perfectly free from trithionate of lead. The lead is now removed by sulphuric acid, any excess of the latter by carbonate of baryta, and the solution of tetrathionic acid evaporated. It may be very highly concentrated without decomposition.

Sulphuretted hydrogen cannot be employed in this case for the separation of the lead, because the sulphuret of lead disengages sulphurous acid from the tetrathionic acid, and the solution of tetrathionic acid is then contaminated with pentathionic acid.

Tetrathionate of Potash.—Iodine is added to a concentrated solution of dithionite of potash (which must contain no sulphite or carbonate) until the red-brown colour no longer disappears. If care be taken to avoid any perceptible heating of the liquid by adding the iodine slowly, but a very minute quantity of the tetrathionate is decomposed into trithionate and sulphur. The tetrathionate of potash is almost wholly precipitated during the preparation, while the iodide of potassium continues in solution. The salt is first extracted with absolute alcohol, and then dissolved in warm water, upon which the solution filtered from the sulphur is mixed with so much alcohol that the precipitate appearing upon each fresh addition slowly redissolves. On cooling, the tetrathionate of potash separates in large crystals; the simultaneously-formed trithionate remains in solution, and can be obtained by a further addition of alcohol or æther, or

by evaporation. Free tetrathionic acid, employed in sufficient quantity, throws down tetrathionate of potash as a granular precipitate from a solution of acetate of potash in alcohol. The tetrathionate of potash can be preserved as a fine powder in the dried state; the large crystals inclose some of the solution of the salt, and this is decomposed in a few weeks into sulphur and trithionate of potash.

Tetrathionate of Soda is obtained in the same manner as the potash salt, but larger quantities of alcohol must be employed to precipitate it from the aqueous solution. It was once obtained by adding to the solution of dithionite of soda neutral perchloride of copper so long as protochloride of copper was separated, and until the solution acquired a faint bluish tint. The salt melts at a gentle heat in its water of crystallization, with separation of sulphur and evolution of sulphurous acid. When tetrathionic acid is saturated with carbonate of soda, or tetrathionate of lead is decomposed with sulphate of soda, there is obtained on evaporation only products of decomposition of the acid—sulphur, sulphate and dithionate of soda.

Tetrathionate of Baryta may be obtained by the addition of an equivalent proportion of acetate of baryta to a solution of tetrathionic acid, the amount of sulphur in which is known, in large tabular crystals, on adding absolute alcohol to the mixture of the solutions of the two salts.

Tetrathionate of Strontia is obtained in the same manner as the preceding salt, but it is more soluble than that in the aqueous liquid mixed with alcohol. It can be procured in thin prismatic crystals by evaporating its solution; but the greater portion of the salt is thereby decomposed into sulphur, sulphurous acid and sulphate of strontia. The analysis of this salt (air-dried) led to the following results:—

Strontia.....	24·78	1	24·74
Tetrathionic acid.....	..	1	49·54
Water	..	6	25·72

Tetrathionate of Lead continually deposits on evaporation, even under the air-pump, crusts consisting of sulphur, sulphate and dithionite of lead, and cannot be obtained in crystals in this manner; but when a solution of acetate of lead is mixed with concentrated tetrathionic acid and alcohol is added, it separates in shining laminæ, which dried in the air afforded on analysis—

Oxide of lead	47·87	1	47·77
Tetrathionic acid.....	..	1	44·53
Water	..	2	7·70

Tetrathionates of Nickel and Cadmium form deliquescent salts, which are procured by decomposing the tetrathionate of lead with the sulphates of the bases, and evaporating the solutions *in vacuo*. Their solutions are not so readily decomposed as that of the pure acid.

Tetrathionate of Copper cannot be obtained in the solid state. On evaporating the solution *in vacuo*, shining brown scales separate

in large quantity, while the solution contains merely sulphuric acid and sulphate of copper.

[To be continued.]

On the Chemical Constitution of Cholesterine. By Dr. Zwenger.

The per-centage composition of cholesterine has been determined by various analysts; but no attempt has hitherto been made to ascertain its true formula, which can only be done by the study of its products of decomposition. When cholesterine is treated with sulphuric acid, it loses its crystalline character, becomes of a reddish colour, and is then converted into a mixture of three different carbo-hydrogens, to which the author gives the common name of cholesteriline, and distinguishes by the letters *a*, *b* and *c*. The three substances are separated from one another by æther, which leaves *a*. cholesteriline undissolved; and the æther on evaporation deposits *b*. cholesteriline in crystals; while the third remains in the mother-liquor. The analysis of these three substances gave the following results:—

	a. Cholesteriline.	*b*. Cholesteriline.	*c*. Cholesteriline.
Carbon	88·05	88·29	87·92
Hydrogen	12·09	12·18	11·99
	100·00	100·00	100·00

These analyses lie within the limits of the error of experiment in several analyses of the same substance; and the carbo-hydrogens might therefore be assumed to be polymeric bodies, and that one only was first formed, and then by the further action of sulphuric acid partially converted into the other two, exactly as occurs in many instances when sulphuric acid acts on carbo-hydrogens. The author, however, has observed that these substances are always formed simultaneously, even when the sulphuric acid is caused to act so as to leave a quantity of cholesterine undecomposed. He considers it more likely, therefore, that their constitution is different, and gives to them respectively the following formulæ:—$C^{32}H^{26}$, $C^{22}H^{18}$, $C^{27}H^{22}$. From the previous analyses of cholesterine he deduces for that substance the formula $C^{81}H^{69}O^{3}$. The action of sulphuric acid consists then simply in removing 3HO when the three carbo-hydrogens are simultaneously produced; thus—

$$C^{81}H^{69}O^{3} - 3HO = C^{32}H^{26} + C^{22}H^{18} + C^{27}H^{22}.$$

—*Ann. der Chem. und Pharm.*, April 1848; and *Monthly Journal of the Medical Sciences* for September 1848.

ANALYTICAL CHEMISTRY.

On the Detection of Lead in the Presence of Bismuth in Blowpipe Experiments. By Edward J. Chapman, Esq.*

It is well known that lead, bismuth and cadmium are the only metals which, when heated before the blowpipe, deposit a yellow

* Communicated by the Author.

coating of oxide on the support. The areola formed by oxide of cadmium is of a much deeper colour than that deposited by either lead or bismuth; and the metal itself is so rapidly volatilized, that in these experiments it is never obtained in the metallic state. When, therefore, in the examination of any substance, a yellow sublimate takes place upon the charcoal with the production of a metallic globule, we have to determine whether this globule consist of lead or of bismuth, or of the two combined. A malleable "button" is usually presumed to consist of lead, and a brittle one of bismuth; nevertheless a perfectly malleable globule may be obtained, containing an admixture of bismuth; and a brittle one, on the other hand, containing a very considerable quantity of lead. For this reason the assay should be examined further; and in the reaction of bismuth with microcosmic salt, as first noted by Berzelius, we possess a ready method of detecting that metal, whether it be combined with lead or not. For this purpose it must be treated with the reagent on charcoal in the reducing-flame, with the addition of a minute particle of tin, when the glass, which is colourless and quite transparent whilst hot, becomes on cooling, if bismuth be present, grayish-black and opake. The only metal which produces a similar reaction is antimony; but this, if it chance to be present, can easily be got rid of by Plattner's process, which consists in fusing the assay matter with vitrified boracic acid in the oxidating flame, taking care not to allow the globule to be entirely surrounded by the flux, by which means the antimony is entirely driven off, whilst the lead and bismuth are retained, as oxides, by the melted acid, and may be again brought to the metallic state by fusion in the reducing-flame with carbonate of soda.

Thus far then the presence of bismuth is easily ascertained even in a malleable globule consisting almost wholly of lead; but the detection of this latter metal in a globule rendered brittle by a large proportion of bismuth, has been hitherto, in experiments with the blowpipe, a much more troublesome affair. Plattner recommends for this purpose a modification of one of the methods given in the Manual of Professor Rose for the separation of lead from bismuth; but this method—which consists, as modified by Plattner, in fusing the mixed metals with an excess of bisulphate of potash, and subsequently treating the fused mass, first with water, and afterwards with nitric acid, to dissolve the sulphate of bismuth—is scarcely admissible in these rapid experiments, in which the use of liquid acids and other bulky reagents should, if possible, be avoided, in order not only to render the operations as simple as accuracy will admit of, but also to prevent the dimensions of the blowpipe-case from affecting its portability. On this account I have endeavoured to discover some other method for the detection of lead when combined in small quantity with bismuth; and the following very simple process for that purpose has occurred to me, founded on the known reduction and precipitation of salts of bismuth by metallic lead—a method which I have found to succeed perfectly with brittle alloys containing upwards of 85 per cent. of bismuth. A small fragment or little

crystal of nitrate of bismuth is placed in a porcelain capsule, and moistened with a few drops of water, the greater part of which is afterwards poured off; and the metallic button of the mixed metals, as obtained by the blowpipe, having been slightly flattened on the anvil until it begins to crack at the sides, is then placed in the midst of the subsalt of bismuth formed by the action of the water, when in the course of a minute, or even less, according to the amount of lead present, minute arborescent crystals of metallic bismuth form and collect around the assay. Copper does not affect this reaction; but if either zinc or iron were present, the precipitation would ensue from that cause alone. Zinc, however, if originally contained in the assay-matter, would be volatilized by the action of the blowpipe, especially if a little carbonate of soda were added to it before subjecting the globule to the above test; and iron might be easily separated by treating the assay in the reducing-flame with a mixture of carbonate of soda and borax—the latter reagent serving to dissolve the iron, and to prevent its reduction to the metallic state. If a single operation do not effect this, the globule must be removed from the saturated dark green glass, and treated with a further supply of the mixture on another piece of charcoal until the resulting glass be no longer coloured.

On the Separation of Antimony from Arsenic. By C. Meyer.

The following method is founded on the insolubility of the antimoniate of soda, and the conversion of arseniferous antimony into arseniate and antimoniate of soda. The author first convinced himself of the perfect insolubility of calcined anhydrous antimoniate of soda. When antimony is deflagrated with nitrate of soda and the mass exhausted with cold water, no antimony can be found in the liquid. The residuous antimoniate of soda is NaO, SbO^5, and anhydrous. When a solution of antimoniate of potash is precipitated with sulphate of soda, and the liquid after some time filtered off clear, no antimony can be detected in it. The crystalline precipitate was proved by analysis to be also NaO, SbO^5, but it contains 6 atoms or 21·23 per cent. of water; experiment gave 21·5. The antimony was estimated in some cases by precipitating it with sulphuretted hydrogen from a solution of the salt in a mixture of muriatic and tartaric acids; in others by the method recently proposed by Rose*, igniting the salt with chloride of ammonium, which gave the most accurate result. This hydrated salt is not quite insoluble in boiling water.

To test the applicability of the insolubility of the calcined antimoniate of soda to its separation from arsenic, a known weight of pure antimony was mixed with arsenic, and the mixture deflagrated with three times its weight of a mixture of nitrate and carbonate of soda. After washing the mass with cold water and ignition, a quantity of antimoniate of soda was obtained, which almost exactly corresponded with the weight which should have been obtained according to theory. On examination before the blowpipe, the salt

* Chem. Gaz., p. 166 of the present volume.

proved to be perfectly free from arsenic. The arsenic was precipitated from the solution with sulphuretted hydrogen, and determined in the usual manner; and its quantity likewise agreed perfectly well with the amount employed.

0·10 grm. tartar-emetic and as much arsenious acid were dissolved in a thick soup, the organic matters destroyed as much as possible by a long-continued current of chlorine, the heated liquid filtered, the mass upon the filter well washed, the solution saturated with sulphuretted hydrogen and left for some time in contact with it; the precipitate filtered, washed, and then dissolved together with the filter in hot nitric acid, the solution saturated with carbonate of soda, some nitrate of soda added to it, the whole evaporated, and the residue heated in a porcelain crucible until the sulphurets and organic matter were completely oxidized, and the mass finally fused. On exhausting the mass with water, 0·057 grm. antimoniate of soda was obtained, while according to theory 0·058 should have been obtained. The solution which contained the arseniate of soda was evaporated to dryness; all the carbonic, nitric and nitrous acids expelled by concentrated sulphuric acid; the salt dissolved in water, mixed with sulphurous acid; and, after expelling the latter, the arsenic precipitated by sulphuretted hydrogen. To separate the free sulphur, the precipitate was dissolved in very dilute ammonia, and reprecipitated with sulphuric acid; it weighed 0·120 grm., which corresponds to 0·096 arsenious acid, which also is very near to the amount employed.

The author applied this insolubility of the antimoniate of soda likewise to the preparation of antimony free from arsenic acid with complete success. Commercial antimony was fused together with $\frac{1}{4}$th its weight of arsenic, the powdered regulus mixed with $1\frac{1}{4}$th part of crude nitrate of soda (cubic nitre), and $\frac{1}{2}$ part carbonate of soda, heated to faint redness, and the mass exhausted with water. The residue of antimoniate of soda was, when dry, fused with half its weight of cream of tartar, when a very beautiful white regulus was obtained, which gave off not the slightest odour of arsenic before the blowpipe, and was characterized by the ease with which it continued to burn away. Moreover the regulus neither contained sodium nor potassium, which latter it generally contains when reduced from the antimoniate of potash.—Liebig's *Annalen*, May 1848.

Method of detecting minute quantities of Opium. *By* M. Hensler.

This method is founded on the reddish-purple colour which porphyroxine gives when heated with dilute hydrochloric acid. In order to employ it, the substance to be tested is mixed with a little potash and agitated with æther. A piece of bibulous paper is dipped several times in the ætherial solution, allowing it to dry between each immersion. It is then moistened with dilute hydrochloric acid, and exposed to the vapour of water, when it acquires a red colour more or less intense according to the quantity of opium present.—*L'Union Médicale*, June 24, 1848; and *Monthly Journal of the Medical Sciences* for September 1848.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Isomeric Conditions of the Peroxide of Tin.
By Prof. H. Rose.

Berzelius first drew attention to the two modifications of the peroxide of tin, one of which is produced by the action of nitric acid upon tin, and the other is precipitated by alkalies from solutions of the perchloride. They are especially distinguished by the first being insoluble in an excess of nitric acid, whilst the latter is readily soluble in it in the cold. Berzelius calls the latter modification the *a*-oxide of tin, and the former the *b*. The other differences mentioned by Berzelius are, that the *a*-oxide dissolves even in dilute sulphuric acid, and is not precipitated from this solution by boiling; whilst the *b*-modification is not dissolved even by concentrated sulphuric acid. Moreover, the modification *a* is readily dissolved by muriatic acid, and is not precipitated by an excess of the acid; it even remains clear on boiling; *b*, on the contrary, is very sparingly dissolved by muriatic acid, but combines with it to form a compound which is insoluble in an excess of muriatic acid; it dissolves however in pure water when the acid is decanted. When this compound is heated to boiling, the oxide is precipitated.

According to Berzelius, both modifications of the peroxide of tin dissolve in the hydrates and carbonates of the fixed alkalies; and when precipitated by acids from these solutions, they possess the same properties as before solution in the alkali. It is however possible to convert one modification into the other by pouring concentrated muriatic acid over moist *b*-oxide, obtained by means of nitric acid, and distilling the whole to dryness at a gentle heat. The distillate contains perchloride of tin, from which *a*-oxide can be prepared; on the other hand, when a solution of perchloride of tin is boiled for some time with nitric acid, *b*-oxide is produced.

This subject has recently been investigated by Fremy. He changes the name of peroxide of tin into stannic acid, as previously proposed by Berzelius, and calls the oxide precipitated by alkalies from the solution of the perchloride stannic acid, and that produced by nitric acid metastannic acid. Besides its insolubility in nitric acid, metastannic acid differs, according to Fremy, from stannic acid principally by the following properties:—It forms salts with potash and soda, which are gelatinous and uncrystallizable, whilst

the soluble stannates crystallize with great facility. It combines, it is true, with muriatic acid, but it does not furnish any compound exhibiting the properties of perchloride of tin; whilst stannic acid easily dissolves in muriatic acid, and again furnishes perchloride; it moreover contains a different amount of water, and the combinations of the two acids with alkalies present a different composition and a different amount of water. Fremy is thence led to compare the two modifications of stannic acid with the various modifications of phosphoric acid, which are distinguished by a different amount of water and by a different capacity of saturation.

The author has long been occupied in investigating the behaviour of the peroxide of tin towards reagents, and has observed phænomena which have entirely altered the views he had arrived at from the results of former experiments. This difficult subject however is far from being exhausted, and the investigations of other chemists will probably lead to different views.

To obtain the *a*-oxide, a solution of the crystallized hydrated perchloride of tin, the preparation of which is very easy, may be used instead of a solution of the volatile perchloride. The author found its composition to be represented by the formula $SnCl^2 + 5HO$, in accordance with the experiments of Lewy.

The most remarkable difference between the two modifications of the peroxide of tin, which the author distinguishes with Berzelius by the letters *a* and *b*, is the total insolubility of the oxide *b* in nitric acid, whilst the oxide *a* dissolves readily in an excess of the same reagent; but the behaviour of the two towards muriatic acid is very different, although not so striking as towards nitric acid; the *a*-oxide dissolves in the cold in an excess of muriatic acid, even when it is concentrated; the modification *b*, as already pointed out by Berzelius, does not dissolve in this acid, though heated with it, but on the addition of water a clear solution immediately results; to obtain this however it is requisite that the oxide should have been heated with the acid previous to the addition of the water.

Every solution of the oxide of tin in acids, especially in muriatic acid, whether it contain the modification *a* or *b*, is precipitated by boiling when sufficiently diluted with water, and the oxide of tin most completely separated. The less free muriatic acid is contained in the solution, and the more it is diluted with water, the quicker does the separation result; it therefore takes place easily from the solution of the perchloride and the hydrated perchloride of tin. The solution of the oxide *b* in muriatic acid usually contains too much free acid, but the whole of the oxide of tin is even precipitated from it by long boiling and renewal of the evaporated water. It even appears that the oxide *b* is precipitated sooner from its solution than the oxide *a* under similar circumstances. When the oxide *a*, whether precipitated by ammonia or by boiling, is dissolved in nitric acid, this solution, when diluted with water, deposits oxide of tin on boiling.

The two modifications of the oxide of tin have exactly the same appearance when precipitated from their solutions by boiling, so that

they cannot be distinguished from one another. They are both bulky. Nevertheless they retain their distinct isomeric character. They both dissolve, under the same circumstances as before, in muriatic acid, the *a*-oxide immediately, the *b* after heating and the subsequent addition of water. In this respect the two modifications of the oxide of tin differ essentially from titanic acid which has been precipitated from its solution by boiling, and which is thereby rendered nearly insoluble in acids.

Ammonia produces bulky precipitates, of the same external appearance, in solutions of the two modifications in muriatic acid; but the resemblance of these precipitates is, as in the case of those produced by boiling, merely apparent. They both retain their peculiarities after precipitation.

The two modifications of the oxide of tin in their solutions in muriatic acid can be distinguished by several reagents. No precipitate is produced by dilute sulphuric acid in the solutions of the oxide *a* if they are not too dilute; whilst those of the oxide *b* are especially characterized by the circumstance that dilute sulphuric acid produces a considerable precipitate in them even when they are mixed with a considerable quantity of muriatic acid; this precipitate is a compound acid—sulphostannic acid. When washed, especially with warm water, the whole of the sulphuric acid may easily be removed, and the *b*-oxide is left behind with its properties unaltered. It dissolves in muriatic acid only when heated with it, and upon the subsequent addition of water. The solution then again furnishes a precipitate with dilute sulphuric acid.

When the sulphate of the oxide *b* is heated with muriatic acid and water is then added, it dissolves, because there is no longer an excess of sulphuric acid in which it is insoluble, but after a time a precipitate forms even in this solution; when therefore the amount of muriatic acid in which the oxide *b* is dissolved is too great, frequently but a very inconsiderable or no precipitate is produced by sulphuric acid. The sulphate of the oxide *b* is soluble in water even after being heated with nitric acid; but in the course of some time a copious precipitate forms in the solution.

But however readily the oxides *a* and *b* may be distinguished in their muriatic solution by their behaviour towards sulphuric acid, it must nevertheless be observed, that when perchloride of tin is diluted with an excessively large amount of water, dilute sulphuric acid is also able to produce a precipitate in this solution; however, it must be diluted with far more water than is usually employed in investigations. The oxide *a*, precipitated in this manner by sulphuric acid, retains its properties.

The author has made numerous experiments with a view to separate quantitatively the two oxides *a* and *b* from their muriatic solution by means of dilute sulphuric acid; no accurate results however were obtained, undoubtedly because the sulphate of the oxide *b* cannot be washed without passing turbid through the filter. The solutions of the two modifications do not behave so differently towards other acids as towards sulphuric acid. A solution of the perchloride

of tin gives no precipitate with muriatic acid; but when the solution of the *b*-oxide in muriatic acid contains no excess of acid, it yields a copious precipitate with muriatic acid, whilst the ordinary solution of the oxide *b*, which always contains a large amount of free acid, affords no precipitate. However, such a solution of the oxide *b* in the least possible quantity of muriatic acid is not always to be obtained, and the author is indebted for it to accident, as will subsequently be seen. The precipitate produced in it by muriatic acid readily dissolves in water after the acid has been poured off. This was to be expected, considering the behaviour of the oxide *b*, obtained by treating metallic tin with nitric acid, towards muriatic acid. It has been previously stated that it is not soluble in an excess of it, not even on boiling, but that it affords a clear solution if, after being heated, a sufficient quantity of water is added.

The muriatic solution of the oxide *b* above mentioned likewise furnishes a precipitate, although only a small one, on the addition of nitric acid; it does not appear immediately, but after some time, and redissolves on the addition of water; but if the oxide *b* has been precipitated by ammonia or by boiling from any muriatic solution, the oxide, after the muriatic acid has been removed, is not soluble in nitric acid, even in the moist, recently-precipitated state; whilst the precipitates of the oxide *a*, produced by boiling or ammonia, are soluble in nitric acid. In the above case, therefore, the presence of the muriatic acid, although not present in excess, is the cause of the slight precipitate by nitric acid.

The ordinary muriatic solution of the oxide *b*, when obtained by treating tin with nitric acid, is distinguished from the solution of the *a*-oxide in hydrochloric acid by several other reactions, besides its peculiar behaviour towards sulphuric acid. If to the solution of the latter tartaric acid be added in sufficient quantity, and then an excess of ammonia, no oxide of tin is precipitated; if, on the contrary, tartaric acid is added to the muriatic solution of the oxide *b*, the presence of this acid has not the least influence on the precipitation of the oxide by an excess of ammonia.

If an excess of a solution of nitrate of silver is added to a muriatic solution of the oxide *a*, the copious white precipitate dissolves entirely in an excess of ammonia. When the solution of the oxide *b* is treated in the same manner, the ammonia dissolves only the chloride of silver, and leaves *b*-oxide of tin behind. It should however be observed, that for the production of the complete solution of the *a*-stannate of silver in ammonia, there must be present a considerable excess of the silver solution. If the solution of the *a*-oxide contains a large quantity of muriatic acid, at first only chloride of silver is precipitated; and if there is not a sufficient quantity of oxide of silver present, the ammonia may separate the *a*-oxide of tin after dissolving the chloride of silver.

Tincture of galls gives no precipitate in a solution of the oxide *a*, but a whitish-yellow one in that of the oxide *b*, which however is not formed immediately, but after several hours.

There are however transitions of the oxide *a* into *b*, and we some-

times meet with solutions of the oxide *b* which do not furnish precipitates with all of the above-mentioned reagents; frequently, for instance, an oxide may be obtained the muriatic solution of which is not rendered turbid by sulphuric acid, but which, after the addition of tartaric acid and ammonia, deposits a very bulky precipitate. This however may also be frequently owing to the presence of too great a quantity of muriatic acid preventing the precipitation by sulphuric acid.

Both modifications of the oxide of tin are soluble in solutions of caustic potash and soda; but both are contained in their unaltered state in the solutions, at least if they have not been kept too long.

Carbonate of potash produces in a solution of the perchloride of tin a very voluminous precipitate with effervescence; the precipitate dissolves entirely in an excess of the precipitant. Oxide *a* is precipitated from this solution by dilute acids, but if the latter are added in large quantity it is entirely redissolved. Carbonate of soda likewise affords a copious precipitate with effervescence in the solution of the perchloride, which however does not dissolve entirely in an excess of the precipitant. However, the turbid solution is rendered perfectly clear by supersaturation with dilute muriatic, sulphuric or nitric acid. Carbonate of potash and soda produce very bulky precipitates in the muriatic solution of the oxide *b*, which are not soluble in an excess of the precipitant; but if the precipitates are washed with water, they are partially dissolved, and the wash-water renders the filtered liquid turbid.

The oxide *a* can be converted in its solutions into the oxide *b*. The direct conversion of the oxide *b* into the *a*-oxide the author has not been able to effect in the moist way; it can only be done by fusion with hydrate of potash.

The author had preserved for a considerable length of time several solutions of the volatile chloride in water in closely-stoppered bottles; on accidentally comparing the properties of one solution, which had been kept for six years, with the freshly-prepared solution of the hydrated perchloride of tin, he found between the two a totally opposite behaviour towards reagents; the first, for instance, gave a copious precipitate with sulphuric acid, the latter none at all. In a solution of the volatile perchloride of tin and of the hydrated perchloride, the oxide *a* is converted by time into the *b*-modification, the transparency of the solution remaining unaffected; however, a long series of years is requisite for this metamorphosis. Two years do not suffice. The solution now exhibits with all reagents the phænomena of a muriatic solution of the oxide *b*, except in one point; for instance, it contains the least amount of muriatic acid requisite to hold the oxide *b* in solution. When it has been obtained by treating tin with nitric acid, and is dissolved in muriatic acid, it requires a much larger quantity. On this account the solution in question, as already stated above, furnishes precipitates with muriatic, and even with nitric acid.

The conversion of the oxide *a* into the oxide *b* may however be produced in a very short time. When a recently-prepared solution

of the volatile chloride or of the hydrated perchloride is heated to boiling, oxide of tin is thrown down; this, as above stated, is the oxide *a*. But when a sufficient quantity of muriatic acid is added to the solution of the perchloride, the precipitation of the oxide by boiling is prevented; it is requisite to boil for some hours, adding from time to time small quantities of muriatic acid, and renewing the evaporated water until a sample of the liquid after cooling is not rendered turbid by sulphuric acid. The other reagents, for instance tartaric acid and ammonia, nitrate of silver and ammonia, as also tincture of galls, now indicate the presence of the oxide *b*.

When the solution of the volatile perchloride or the hydrate is mixed with nitric acid and boiled uninterruptedly for some time, the tin at last separates as *b*-oxide; but this separation does not result until nearly the whole of the muriatic acid has been expelled.

When the oxide *a* is dried at the ordinary temperature, it dissolves readily and wholly in cold muriatic acid; the solution then still exhibits all the properties of the oxide *a*; if it be dried at an elevated temperature, for instance that of boiling water, the greater portion remains undissolved, but what does dissolve furnishes no precipitate with sulphuric acid. The oxide still decreases in weight up to 338°, but no further when heated above that temperature.

When crystallized protochloride of tin has been kept in the solid state for several years exposed to the air, it has become entirely converted into a combination of perchloride of tin with peroxide, but the tin is contained in the compound in the form of the oxide *a*; the presence of water is therefore necessary to produce with time the metamorphosis of the oxide *a* into the oxide *b*.

A solution of the oxide *a* in potash can however be very soon converted into the oxide *b*. When protochloride of tin is dissolved in hydrate of potash, and the filtered solution exposed for some time to the air, the protoxide is gradually converted into peroxide; it is contained in the solution as the modification *a*; but if the solution is exposed still longer to the air, it becomes turbid, and deposits the whole of the peroxide of tin in proportion as the potash becomes converted into carbonate; the deposit, however, is the *b*-oxide.

Besides the two modifications of the peroxide of tin *a* and *b*, several others must be distinguished. Both behave differently towards muriatic acid, but they are soluble in it; but when the two modifications are heated to redness, they are rendered insoluble in muriatic acid; they even resist the action of concentrated sulphuric acid, and are not rendered soluble in water by fusion with bisulphate of potash. The calcined peroxide of tin, which has all the properties of the native tin-stone, must contain some other modification than the oxide *a* or *b*. The author is inclined to admit another modification besides that existing in calcined oxide of tin; it is the one which is produced by fusion with carbonated alkalies. Of the fused mass, some stannate, but not a very large amount, dissolves in the water, along with the free carbonated alkali; the oxide contained in it is the modification *a*, but that which has been left undissolved cannot be washed with water when nearly the whole of the alkaline carbonate has been

removed, but passes quite milky through the filter. Muriatic acid dissolves but very little of what has been left undissolved by the water, and even concentrated sulphuric acid is almost without action upon it. It is difficult to decide whether the insoluble portion essentially contains alkali, and is a very acid stannate or not, for it is quite impossible to separate the suspended oxide of tin from the solution, in which some carbonate is still dissolved; it can however be brought so far that no alkali can be detected in it; so that the insoluble oxide must be nearly free from it.

Fremy states that the solution of the oxide *b* produced by nitric acid does not yield perchloride of tin with muriatic acid, while the oxide *a* readily furnishes perchloride. The author's experiments did not confirm this. When the muriatic solutions of the two are distilled, water and muriatic acid first pass over, and subsequently anhydrous perchloride of tin is volatilized; but even the first traces of acid water obtained contain oxide of tin, which was volatilized as chloride; so that it is not advisable in quantitative analyses to concentrate a dilute muriatic solution of peroxide of tin by evaporation.

The author is not inclined to deduce the differences of the two kinds of oxide of tin from their different capacity of saturation as acids, as in the case of the several modifications of phosphoric acid. If such is really the case, as asserted by Frémy, on which point however the author has not made any experiments, it is owing to the different state of the two oxides, and is the effect and not the cause. If we consider to what an extent several metallic oxides are capable of changing their densities when exposed to different temperatures, are consequently capable of forming after calcination in the anhydrous state various isomeric modifications, there is no apparent reason why similar isomeric states should not also obtain with the oxides in their combinations and solutions in water.—*Proc. of Royal Berlin Academy*, June 1848.

Creatine a Constituent of Human Flesh. By Dr. Schlossberger.

The existence of creatine in human flesh not having been yet ascertained, although it is found in the urine, the author treated 6 lbs. of human flesh by the usual process, and extracted from it a quantity of creatine, amounting in all to about 2 grms., a proportion approximating very closely to that obtained by Liebig for the quantity existing in ox- and horse-flesh. Dr. Schlossberger did not obtain the slightest trace of inosinic acid in this experiment.—*Ann. der Chem. und Pharm.*, April 1848; and *Monthly Journal of the Medical Sciences* for September 1848.

Chemical Examination of Chalk-Stones.
By Thornton J. Herapath, Esq.*

The bodies commonly called chalk-stones are, as is well known, the concretions which are sometimes formed in the cavities of the

* Read before the Bristol Philosophical and Literary Society, September 28th ult., and communicated by the Author.

joints, in the bursæ mucosæ, &c., of gouty patients. The first, and, as I believe, the only analysis of these which has been published, was made by Dr. Wollaston in 1797*, who found them to be principally, if not entirely, composed of urate of soda. This statement has been copied into several of our more recent works on chemistry and pathology, without any apparent efforts having been made by their authors to confirm it by a repetition of his experiments. Several fine specimens of this formation having been presented to my father, a short time since, by a friend, I was induced, at his desire, to again subject them to analysis, in order to see whether their composition was really that assigned to them by Wollaston, or whether it differed in different individuals. The results of this examination form the subject of the present paper.

The stones which were submitted to analysis had been extracted about three years ago from the finger-joints of Mr. A—— of Bristol, a gentleman about sixty years of age, who has them to such an extent as to have almost lost the use of his hands and arms. They varied greatly both in size and shape, some being not larger than a pea, and nearly spherical, while others, on the contrary, were from three-quarters of an inch to an inch and a half in length, and more or less irregularly ovoid.

They were exceedingly soft and friable, so as to admit of their being easily cut with a knife. The section exhibited none of the concentric circles so evident and well-marked in most urinary and biliary calculi. They were not, however, perfectly homogeneous in composition, as upon examination with a microscope of low power numerous gritty, or rather crystalline particles could be perceived, which were considerably harder than the surrounding mass.

I found the specific gravity of one of the largest specimens to be about 1·5771. This estimation, however, is somewhat below the truth, from the numerous minute bubbles of air contained in the cavities of the concretion, which it was impossible to remove entirely even by means of an exhausting syringe.

Cold water had very little, if any, action on them; but water at 212° F. dissolved a small quantity, which was nearly all deposited again upon cooling. Boiling æther and alcohol took up a little of a fatty body, having a great resemblance to human fat, which it probably was.

A concentrated solution of caustic potash had little or no effect upon them; but when diluted, and with the assistance of heat, it dissolved a considerable quantity, the greater proportion of which was again precipitated upon the addition of an acid in excess.

Ammonia, even when hot, had no further action upon them than that of saponifying the small quantity of fat they contained.

When treated with the diluted mineral acids, they were decomposed, giving a solution from which an excess of ammonia produced an abundant whitish precipitate, which was nearly wholly redissolved by acetic acid in excess. The filtered solution likewise contained lime and soda, with traces of potash.

* Phil. Trans. 1797, p. 386.

The white insoluble substance that was left upon treating the powdered calculus with an acid, when boiled in a strong solution of biborate of soda, almost entirely dissolved, leaving a slight residue of albumen.

Upon heating some of the powdered concretion with concentrated nitric acid, a slight effervescence took place, and the solution, when evaporated to dryness, furnished a residue of a fine pink colour, which was turned to a bright crimson-red upon the addition of ammonia.

The organic portion of the calculi was therefore almost entirely composed of uric acid.

When heated to redness upon a piece of platina-foil, they burnt with a bright smoky flame, leaving a carbonaceous residue, which, upon further incineration, left about half its weight of a white ash. This, to my astonishment, when treated with boiling water, gave a solution that consisted principally of phosphate of soda, with traces only of carbonate of soda. By repeating the experiment, however, at a lower temperature and with greater precautions, an ash was obtained which contained a much larger proportion of carbonated alkali. The insoluble residue was composed for the most part of phosphate, with some carbonate of lime.

The phosphate of lime must, therefore, in the first experiment have been decomposed by the carbonate of soda, giving rise to phosphate of soda and carbonate of lime. This will show how necessary it is for chemists to pay attention to the temperature at which they incinerate, in determining the inorganic constituents of organic bodies.

Upon a quantitative analysis, they were found to contain in 100 grs. as follows:—

Fat	1·123
Chloride of sodium, Phosphate of soda, Extractive matter, Albumen	a little.
Urate of soda, with some urate of potash	43·973
Urate of lime	14·769
Phosphate of lime	34·141
Perphosphate of iron	traces
Water and loss	5·994
	100·000

This analysis, when examined in a medical point of view, will explain the reason why the various substances which have been from time to time proposed by medical men as remedies for these calculous diseases, have been found to be perfectly useless when brought into practice; for until some common solvent shall be discovered for both uric acid and phosphate of lime, gout and its concomitants must still be endured by frail mortality. For even should the opinion recently promulgated by Dr. Alexander Ure* prove correct, that the

* Med. Chir. Trans., vol. xxiv.

internal administration of benzoic acid, or an alkaline benzoate, will convert uric into hippuric acid (which Prof. Liebig and others have since appeared to contradict), still this remedy would only act as a prophylactic, and would not, in my opinion, remove concretions already deposited in the tissues.

As I thought it would be interesting to discover whether the uric acid from these concretions had the same composition as that obtained from other sources, I subjected some, which had been repeatedly purified, to an ultimate analysis:—

I. 4·03 grs., burnt with chromate of lead, with the necessary precautions, gave 5·319 grs. of carbonic acid and 0·857 gr. of water.

II. 3·91 grs., burnt with chromate of lead, gave 5·086 grs. of carbonic acid and 0·807 gr. of water.

III. 5·00 grs., burnt with potash and lime by Varrentrapp and Will's process, gave 11·715 grs. of metallic platinum.

These analyses give the following composition per cent.:—

	I.	II.	III.	Mean.	Atoms.	Calc.*
Carbon	35·997	35·476	..	35·736	10	35·714
Hydrogen ..	2·361	2·294	..	2·327	4	2·380
Nitrogen ..	..	..	33·634	33·634	4	33·335
Oxygen	..	..	..	28·303	6	28·571

which agrees very closely with that obtained by Prof. Liebig† in his analysis of the uric acid from the excrements of animals, as will be seen upon comparing the following numbers with those given above:—

Carbon	36·082
Hydrogen	2·441
Nitrogen	33·361
Oxygen	28·126

Mansion House, Old Park, Bristol,
September 12th, 1848.

On the Preparation, Properties and Composition of the Polythionic Acids and their Salts. *By* F. Kessner.

[Continued from p. 373.]

III. *Preparation of Pentathionic Acid.*

This acid was prepared in general according to Wackenroder's process, but with this modification, that when the original solution of sulphurous acid had been saturated with sulphuretted hydrogen, sulphurous acid was again passed into it, and then sulphuretted hydrogen, until a considerable deposit of sulphur covered the bottom of the vessel. The clear liquid was decanted; it contained some sulphuric acid, which was removed by carbonate of baryta, when any sulphur suspended in the liquid was at the same time precipitated with the sulphate of baryta. The clear acid could be concentrated in the water-bath without decomposition to a specific gravity

* C=6, H=1, N=14, O=8. † Ann. de Chim. et Phys., lv. p. 58.

of 1·25–1·30. The further concentration must be effected at a gentle heat, and finally *in vacuo*; it may thus be obtained of a specific gravity 1·6.

When dithionite of lead is slowly added to water into which a brisk current of sulphuretted hydrogen is passed, not adding a further quantity until the preceding has become perfectly black, the liquid becomes acid, deposits, as formerly stated by Persoz, but a very small quantity of sulphur, and contains, as far as can be judged from its properties, pentathionic acid.

When recently-precipitated sulphuret of lead is added to solutions of pentathionic and tetrathionic acids, they immediately give off the odour of sulphurous acid, and the liquid becomes turbid. The same therefore also occurs when the sulphuret of lead, which separates in the treatment of dithionite of lead with sulphuretted hydrogen, is left too long in contact with the mother-ley. This explains a former statement of Pelouze, which apparently contradicts the observation made by Persoz, the former asserting that, in the supposed separation of dithionous acid from its lead salt, the acid was spontaneously decomposed as in the free state.

In other respects the origin of the pentathionic acid from dithionite of lead is exactly the same as in the mode of preparation according to Wackenroder. The dithionous acid is not eliminated from its lead salt in the form of an isomeric modification as pentathionic acid; but it separates unaltered, is then decomposed as usual into sulphurous acid and sulphur, and the sulphuretted hydrogen gas forms with the sulphurous acid pentathionic acid; this accounts for the sulphuret of lead which separates constantly being mixed with free sulphur. The sulphite of lead is probably equally well adapted for the preparation of the pentathionic acid as the hyposulphite.

IV. *Behaviour of Pentathionic Acid towards Bases.*

The author has made the following experiments on this subject. Pentathionic acid, prepared according to Wackenroder's method and concentrated until it possessed a specific gravity of 1·32, was poured into a solution of acetate of potash in alcohol of 0·811 spec. grav. The precipitate, after being washed with alcohol, was dissolved in warm water, filtered from the separated sulphur, the quantity of which was pretty considerable, and the solution further treated with alcohol, as in the preparation of tetrathionate of potash. The salt which separated on cooling had the properties of the tetrathionate, and not those of the pentathionate of potash. The following analyses I.–IV. are of a salt which was prepared according to Wackenroder's method; the analyses V.–VII. were made with a salt which had been obtained by decomposing hyposulphite of lead with sulphuretted hydrogen:—

	I.	II.	III.	IV.	V.	VI.	VII.		
Potash....	31·01	..	..	..	30·78	30·91	..	1	31·18
Sulphur ..	..	43·08	43·28	43·05	..	..	43·28	4	42·35
Oxygen ..	..	..	..	..	..	..	..	5	26·47

Equal parts by weight of the acid of 1·47 spec. grav. and crystal-

lized acetate of baryta were dissolved in water and precipitated with absolute alcohol; the separated salt was dissolved in water, filtered from sulphur, and the solution again precipitated with alcohol. This salt still exhibited the reactions of the pentathionate of baryta after it had been kept for three months. The air-dried salt afforded on analysis—

Baryta	34·61	2	34·81
Sulphur.....	32·79	9	32·71
Oxygen.....	..	10	18·17
Water	..	7	14·31

From these numbers it results that the salt is identical with that described by Ludwig* as tetrapentathionate of baryta; the author however does not regard this product as a definite compound, but rather as a mixture of the two components.

So much is certain, from what is hitherto known of this acid, that free acid prevents the decomposition of the pentathionic acid and any elimination of sulphur, whilst free alkali readily converts it into tetrathionic, and this again into trithionic acid.

V. *Reactions of the Polythionic Acids and their Salts.*

Trithionate of Potash is gradually decomposed by boiling its solution in water into sulphur, sulphurous acid and sulphate of potash. The odour of the sulphurous acid is perceived sooner than the turbidness produced by the eliminated sulphur. With the isolated acid this decomposition takes place more rapidly, for instance when muriatic acid is added to the solution of the salt; no sulphuretted hydrogen can be discovered in this case, but it is detected by means of paper which has been moistened with basic acetate of lead among the vapours given off when the dry salt is treated with concentrated muriatic acid.

Tetrathionate of Potash and Tetrathionic Acid are not decomposed by boiling their solutions; both differ moreover from the preceding bodies in their solutions disengaging sulphuretted hydrogen on the addition of muriatic acid and the application of a very gentle heat. Moderately-concentrated pentathionic acid, on boiling, smells faintly of sulphur, and on the addition of muriatic acid, of sulphuretted hydrogen. Tetrathionic and pentathionic acids only disengage sulphurous acid when they are highly concentrated, or when they are deprived of water by means of sulphuric acid. The potash salts of the two acids, S^3O^5 and S^4O^5, are not decomposed at 257°, but at 266° they disengage sulphur and sulphurous acid.

Caustic Potash converts both the free and combined trithionic acid into dithionite and sulphate of potash; and consequently on the subsequent addition of acetate of lead, no precipitate of sulphuret of lead is formed, as on the similar treatment of tetrathionic and pentathionic acids,—a portion of their sulphur combining with the alkali to form sulphuret of potassium.

Sulphate of Copper in excess, heated with trithionic acid, imme-

* Chem. Gaz., p. 12 of the present volume.

diately deposits persulphuret of copper. With the other two acids there is only a brown precipitate formed after very long boiling.

Protonitrate of Mercury instantly produces a black precipitate of protosulphuret of mercury in a solution of trithionic acid, but yellow precipitates in solutions of the two other acids, which do not change in the cold, and turn black very slowly on boiling. These precipitates are probably combinations of the persulphuret of mercury with the protosulphate, and contain in the case of the pentathionic acid some free sulphur. When trithionic acid is contained in the tetrathionic or pentathionic acid, the precipitate produced on the addition of the first drops of the reagent varies from gray to black.

Perchloride of Mercury instantly yields with trithionic acid a perfectly white precipitate, and with the other two acids gradually somewhat yellowish precipitates, which are the well-known combinations of the perchloride of mercury with persulphuret. The precipitates furnished by the tetrathionic and pentathionic acids moreover contain an admixture of sulphur.

Percyanide of Mercury produces in solutions of all three acids, and in those of the salts of trithionic acid, yellow precipitates; but, on the other hand, no change in solutions of the tetrathionates, except after some days or on boiling, when it affords a black precipitate.

Nitrate of Silver immediately affords a white precipitate with trithionic acid, and a yellow one with the other two acids; all these precipitates soon become black.

Ammoniacal Nitrate of Silver, or *Percyanide of Mercury*, as likewise *Sulphuretted Hydrogen*, produce no change in solutions of trithionic and tetrathionic acids supersaturated with ammonia; when, on the other hand, pentathionic acid is quickly mixed with ammonia, an ammoniacal solution of silver soon strikes a brown colour, which grows darker and darker, and sulphuret of silver is deposited; ammoniacal solution of percyanide of mercury gradually produces a black precipitate of sulphuret of mercury, and sulphuretted hydrogen a separation of free sulphur.

VI. *Estimation of the Oxygen in the Polythionic Acids.*

The method which the author employed to analyse the polythionic acids is based upon the properties which they possess of being decomposed in such a manner by salts of copper, silver and peroxide of mercury, that only sulphuric acid and metallic sulphuret, and in some cases also free sulphur, constitute the products of decomposition, but not sulphurous and hyposulphuric acids; consequently when the amount of sulphuric acid contained in the solution, and the quantities of metal and sulphur in the precipitate, are determined, we possess three elements for the calculation of the sulphur and oxygen in the polythionic acids. We may here consider the oxygen of the metallic oxide without hesitation to be consumed in oxidizing one portion of the polythionic acid to sulphuric acid, while the other portion of the polythionic acid is decomposed into sulphur and sulphuric acid. We have therefore merely to deduct an amount

of oxygen equivalent to the metal found from the oxygen of the found sulphuric acid, to ascertain the amount of oxygen in the polythionic acid.

Taking into consideration the properties of the sulphurets of the above-named metals, and the behaviour of their salts when added in excess towards these sulphurets, it will be found that the cyanide of mercury, which does not combine with the sulphuret of mercury, is alone suited for the present object.

The polythionic acids and their salts are very rapidly decomposed when their solutions are boiled in small long-necked flasks with a sufficient quantity of cyanide of mercury; prussic acid is given off, but no sulphocyanic acid is formed. The dithionites, at least the alkaline salts, are decomposed with great difficulty, and only imperfectly, by the same salt; nevertheless they may be analysed in the same manner if to the solution of these salts, mixed with the percyanide of mercury, nitric acid of 1·2 spec. grav. is added in drops, which produces a yellow precipitate, boiling after each drop, until it becomes black. It may easily be seen that the decomposition is complete by the analysis, since the equivalent of sulphuret of mercury is nearly identical with that of the sulphate of baryta (116 and 116·5). On using acetic acid (even a large excess), instead of nitric acid, 4 per cent. too much of mercury is obtained, and 2 per cent. too little sulphate of baryta.

In the precipitate produced by boiling with cyanide of mercury, the mercury must be separately determined, as it very frequently contains free sulphur. In this investigation the dry precipitate was collected upon a weighed filter, and its weight determined; the filter, together with the precipitate, was then boiled with nitric acid, with the addition of muriatic acid, and subsequently of chlorate of potash, until the whole of the sulphur had dissolved, which was then determined as usual as sulphuric acid. From this the sulphur was calculated, and the mercury estimated by the loss; the following analyses are made according to this method:—

Analysis of amorphous trithionate of potash, dried over sulphuric acid:—

Potash.....	34·71	..	..	1	34·87
Sulphur	..	35·78	35·60	3	35·53
Oxygen	..	..	29·70	5	29·60

Analysis of tetrathionate of potash, dried over sulphuric acid:—

Potash.....	31·11	..	1	31·18
Sulphur	..	42·54	4	42·35
Oxygen	..	26·60	5	26·47

Analysis of an aqueous solution of pentathionic acid.—Following the above method, three analyses (I., IV., VII.) gave the weight of the oxygen at exactly half that of the sulphur, proving that the acid must contain equal equivalents of sulphur and oxygen. Several sulphur determinations are arranged in the following table, together with the specific gravities of the solutions:—

	Spec. grav. at 72° F.	Per-centage of sulphur.	Anhydrous acid.	Per-centage of water.
I.	1·2334	21·41	32·11	67·89
II.	1·2334	21·29	31·93	68·07
III.	1·2334	21·43	32·14	67·86
IV.	1·3196	27·77	41·65	58·35
V.	1·3196	27·90	41·85	58·15
VI.	1·4735	37·32	55·98	42·02
VII.	1·5062	39·78	59·67	40·33

With respect to the sulphur determinations, it should be observed that the quantity contained in the generated sulphuric acid is, according to the above method of analysis, in the following proportion to that contained in the black precipitate:—

In the trithionic acid as ..... 2 : 1
In the tetrathionic acid as ..... 2 : 2
In the pentathionic acid as ..... 2 : 3

The oxygen contained in the sulphuric acid amounted in all cases to 6 times the oxygen corresponding to the mercury, showing that there are always formed 2 atoms of sulphuric acid to 1 of sulphuret of mercury, and that any other sulphur present is separated without any further action as such. The decompositions of the polythionic acids by cyanide of mercury may be expressed in the following manner:—

$$S^3O^5 + HO + HgCy = 2SO^3 + HgS + HCy$$
$$S^4O^5 + HO + HgCy = 2SO^3 + HgS + S + HCy$$
$$S^5O^5 + HO + HgCy = 2SO^3 + HgS + 2S + HCy$$

Whilst the dithionous acid is decomposed by cyanide of mercury in the following manner:—

$$S^2O^2 + HO + HgCy = SO^3 + HgS + HCy$$

Whence it results that the hyposulphurous acid not merely differs from the pentathionic acid in the number, but also in the arrangement of the atoms.—Poggendorff's *Annalen*, lxxiv. p. 249.

Observations on Asparagine.
By V. Dessaignes *and* J. Chautard.

The authors, who appear to be unacquainted with Piria's researches* on the same subject, found asparagine in the young shoots of peas, beans, lentils and French beans, which had been sown in a cellar (Piria showed that vetches which had germinated exposed to the light of day contained, up to the period of their flowering, as much asparagine as those grown in the dark). 83 grms. of asparagine were obtained from 9 quarts of the juice of pea-shoots. The results of the analyses agree with those existing. 1·35 quart of juice from the shoots of French beans contained 7·4 grms. asparagine. The stems of the vetch which had been grown in the dark

* Chem. Gaz., page 129 of the present volume.

upon moist tow contained as much as those grown in soil also in the dark,—about 27 grms. in 3 quarts of juice.

In some shoots from dahlia tubers kept in a cellar, and also in the tubers themselves, asparagine was found on evaporating the expressed juice after straining from the inuline.

The hot solution of asparagine readily dissolves oxide of silver; the colourless solution evaporated in the dark over sulphuric acid furnished groups of black crystals, but yellowish-brown by transmitted light; they afforded 48·94 per cent. of silver; the formula $C^8 H^7 N^2 O^5 + AgO$ requires 48·53. Asparagine expels acetic acid from acetate of lead at a boiling temperature, but is very slowly effected; on evaporation a gummy mass is obtained. Oxide of zinc dissolves very easily in a boiling solution of asparagine; on evaporation, white laminar crystals are obtained, which lost a considerable quantity of water at 212°, and after drying afforded 25·17 per cent. oxide of zinc; the formula $C^8 H^7 N^2 O^5 + ZnO$ requires 24·77 per cent. With respect to the behaviour of asparagine towards acids, the authors observed that asparagine dissolved in an equivalent of sulphuric acid which had been diluted with water, and that on evaporation free asparagine first crystallized, leaving behind a solid amorphous mass.

The following statements of the authors are of considerable interest. Notwithstanding the neutral reaction of asparagine, it behaves towards some bases as a faint acid; in this respect it resembles several other organic substances, which are nevertheless not acids; such is the case with sugar of gelatine, urea, &c., which combine with bases, acids and salts. Thus, on evaporating a solution of 1 equiv. $C^8 H^8 N^2 O^6$ and 2 equivs. nitrate of silver, a crystalline salt was obtained, which, dried at 212°, furnished 45·78 and 45·71 per cent. of silver. It could be recrystallized without experiencing any change of form. The amount of silver corresponds to the formula $C^8 H^8 N^2 O^6 + 2(AgO, NO^5)$. On taking nitrate of lead instead of the silver salt, a gummy mass was obtained.

Among the different plants sown in the same cellar and in the same soil, which contained perceptible quantities of nitrates, especially nitrate of lime, no asparagine was found in the pumpkin, buckwheat and oats, but nitrate of potash; in the shoots of French beans, which contained but a small quantity of asparagine in their juice, nitre occurred. Nitre was likewise found in the sprouts of potatoes, but no asparagine; on the other hand, those plants which afforded asparagine contained no nitre. The authors here observe, that crystals of the ammonio-phosphate of magnesia were found in the putrefying juice of lentils.

Peroxide of mercury dissolves readily in a warm solution of asparagine; the solution is colourless; when concentrated, water produces a white precipitate in it. It dries to a gummy mass, which assumes a gray colour at 212° and puffs up. The authors have not ascertained what becomes of the organic substance. The gray colour was owing to reduced mercury.

The authors also describe a crystalline compound of asparagine

with oxalic acid, which is formed on dissolving equivalent proportions of the two substances in water.

Two kinds of crystals were obtained on evaporation; crystals of asparagine coated the bottom of the vessel, while some white crystalline masses covered the margin; on decomposing the latter with chalk, as large an amount of asparagine was obtained on evaporation as crystallized spontaneously; the compound is consequently $C^2 H^3 O^6 + C^4 H^5 NO^4$. After being kept for twenty-four hours *in vacuo* over sulphuric acid, the salt had lost 3 equivs. water, and was now represented by the formula $C^2 HO^4 + C^4 H^4 NO^3$, which composition was also confirmed by the determination of the amount of oxalic acid. According to this compound, the formula of the asparagine must be halved, and we shall have—

Crystalline asparagine	$C^4 H^4 NO^3 + HO$
Ditto dried at 212°	$C^4 H^4 NO^3$
Asparagine and potash.....	$C^4 H^4 NO^3 + C^4 H^3 NO^2 + KO$
Asparagine and oxide of copper ..	$C^4 H^4 NO^3 + C^4 H^3 NO^2 + CuO$
Asparagine and oxide of silver ..	$C^4 H^4 NO^3 + C^4 H^3 NO^2 + AgO$
Asparagine and oxide of zinc	$C^4 H^4 NO^3 + C^4 H^3 NO^2 + ZnO$
Nitrate of silver and asparagine ..	$C^4 H^4 NO^3 + NO^5 + AgO$
Oxalate of asparagine	$C^4 H^4 NO^3 + C^2 HO^4$

In conclusion, the authors observe that chlorine, even in diffused light, soon destroys the asparagine. Peroxide of lead expels ammonia without producing aspartic acid.—*Journ. de Pharm.*, xiii. p. 245.

On a new Alkaloid—Pseudoquinine. *By* M. MENGARDUQUE.

M. Pelouze possessed in his laboratory an extract of bark of unknown origin, which he gave to me for examination. It formed a dark reddish-brown friable substance, extremely bitter, sparingly soluble in water, but soluble in acids, which it saturated, yielding true saline solutions, from which water precipitated it as a pitchy mass. This substance, treated by the processes described for the extraction of quinine and cinchonine, furnished not a trace of either of these alkaloids, nor could I detect in it any of the cinchovatine of M. Manzini; but I found an alkaloid, which I suspect to be new, and which I have been able to define to the satisfaction of M. Pelouze.

This alkaloid differs from the substance which accompanies it in the extract from its saturating acids better; to such a degree, in fact, that it expels ammonia from its combinations in the same manner as lime or baryta; and from its being scarcely soluble in æther even on boiling. These properties were turned to account in preparing it; the extract was boiled with its weight of hydrochlorate of ammonia until it no longer disengaged ammonia. On cooling, a very considerable brown deposit, of a syrupy consistence, was formed, and the supernatant liquid was clear and of a slight amber tint. This liquid, after decantation and filtration, was precipitated by am-

monia; it afforded yellowish flakes, which became soft and agglutinated by heat. It was dried and treated with cold æther, which dissolved the greater portion, leaving the new alkaloid in a pure state as a white powder.

Thus purified, it exhibits the following characters:—It melts when heated upon platina, then burns with a blue flame, leaving no residue. It is insipid, insoluble in water, soluble in alcohol, more so in hot than in cold; it crystallizes readily from its alcoholic solution in irregular prisms; it dissolves in mineral and organic acids, even dilute, but is insoluble in æther. Ammonia, potash and soda precipitate it from its saline solutions; water separates it from its solution in alcohol. When dissolved in chlorine water, the liquor assumes a yellowish-red colour on the addition of a few drops of ammonia; under the same circumstances quinine yields, as is well known, a green solution.

Its solution in sulphuric acid is neutral to test-paper, slightly bitter, and furnishes on evaporation beautiful flat prisms. Its solution in hydrochloric acid exhibited all the characters of a hydrochlorate, but could not be obtained in crystals. It furnished on elementary analysis—

Carbon	76·5	76·7
Hydrogen	8·1	8·2
Nitrogen	10·2	10·4
Oxygen	5·2	4·7

Comptes Rendus, August 21, 1848.

On the Occurrence of Urea in the Vitreous Humour of the Eye.

Millon has recently detected the occurrence of urea in the vitreous humour of the eye. This statement has since been confirmed by Prof. Marchand and Prof. Wöhler, who obtained a notable quantity from fifty calves' eyes.—Liebig's *Annalen*, lxvi. p. 128.

ANALYTICAL CHEMISTRY.

On a new Method for the Detection of Iodine and Bromine. *By* Dr. G. L. Cantu, Professor of Chemistry in the Royal University of Turin*.

Since the discovery of iodine in the mineral waters of Italy, the chemists of various countries prosecuting the same inquiry have proposed various methods more or less capable of detecting the presence of this element when existing in minute quantity.

That which I am about to describe appears to me to be not unworthy the attention of chemists, inasmuch as, being most eminently calculated for the detection of the smallest quantities of iodine, it at the same time demonstrates the presence of bromine. In fact, by using it, I have succeeded in discovering these two substances in all

* Communicated by T. H. Henry, F.R.S.

the mineral waters, and in nearly all the potable waters of Piedmont, as well as in those of the principal rivers; and lastly, in the celebrated mineral waters of Vichy in France and of Louêche in Switzerland, in which the most expert chemists had hitherto sought for it in vain.

The process is shortly as follows:—The water under examination is evaporated in a porcelain capsule to about half its bulk; carbonate of potash, of absolute purity, is then added (I say absolute purity, as the ordinary carbonate of potash contains sensible traces of iodine and bromine*) in slight excess, and boiled for some time in order to decompose the earthy salts contained in it; the liquid is allowed to become cool, and is then filtered; it is now evaporated to dryness, taking care however not to heat the saline matter too highly in the desiccation; the residue, if in small quantity, is powdered in the same capsule, and is treated with alcohol of 40°, in order to separate the salts soluble in this menstruum, among which will be found the bromides and iodides if they existed in the water. The liquid is evaporated to dryness at a gentle heat; and if it contain organic matter, as is generally the case, this is destroyed by ignition at a low red heat; a few drops of dilute acetic acid are next added in such proportion as to be in slight excess, taking care that the small quantity of carbonate of potash taken up by the alcohol is dissolved and neutralized. It is now again evaporated to dryness, to expel the excess of carbonic acid, avoiding a degree of heat that would decompose the acetate of potash, as this would communicate a brown tinge to the liquid and obscure the action of the test. At this point the residuary matter is dissolved in the smallest possible quantity of pure water, with two or three drops of a weak solution of starch recently prepared. This being done, a small quantity of the test-liquor (consisting of a mixture of 10 parts of sulphuric acid of 66° with 1 part of nitric acid of 25°) is placed in a glass with a narrow base; then the solution of the saline residue is poured very gently down the side of the glass so as to rest on the test-liquor without mixing with it. By operating in this manner, if iodides or bromides existed in the water, and the coexistence of these substances is almost constant, there will quickly appear two zones in the saline solution, one of a clear topaz-yellow, sometimes inclining to green, and the other of a blue colour, floating on it.

I believe it to be unnecessary to point out the theoretical reasons of this reaction, as they will be obvious to all cultivators of the science. I will only mention *en passant*, that the perfection that I imagine I have brought this test to, is the result of some researches I have made on the action of nitrogen and oxygenized bodies, on

* To obtain carbonate of potash free from chlorides, bromides and iodides, it is necessary to proceed in the following manner:—Bitartrate of potash, colourless and crystallized, is calcined to whiteness, the residue treated with distilled water, and the solution evaporated to the consistence of syrup; alcohol of 40° (Beaume?) is then added, agitating thoroughly the mixture, and allowing it to react for some time, the alcoholic liquor being afterwards decanted; the saline residue is brought on a filter, and washed with alcohol until a portion of the latter, being evaporated to dryness and examined with the proper tests, no longer gives any indication of the presence of iodides, bromides or chlorides.

the haloid salts, and also on the mutual reaction of fluorides, chlorides, bromides and iodides under the influence of an elevated temperature, when the latter of these has a more electro-positive metal for its base than the one preceding it.—*Raccolta Fisico-Chimica Italiana*, No. xxviii., 1848.

On the Preparation of Meta-antimoniate of Potash as a Test for Soda. By M. Fremy.

The author observes, that since the publication of his first memoir on the antimoniates, the meta-antimoniate of potash has been generally employed in laboratories as a test of the salts of soda; and as the preparation of this salt has been found difficult by several chemists, the author states the following to be the process which he now employs, and by which he obtains in a few hours nearly two pounds of meta-antimoniate of potash.

He begins by acting upon one part of antimony with four parts of nitre in a red-hot earthen crucible; insoluble anhydrous antimoniate of potash is formed, which is washed with cold water to remove the nitrite and nitrate of potash, an excess of which it usually retains.

The antimoniate of potash is then boiled for two or three hours in water, in order to convert it into the gummy soluble antimoniate; water is to be added to supply the loss by evaporation. During ebullition the greater part of the antimoniate dissolves, there remaining but a small quantity of bi-antimoniate of potash, which is separated by the filter.

The solution of the gummy antimoniate of potash is then evaporated, adding to it several fragments of pure hydrate of potash so as to render it very caustic. A few drops of the solution are tried from time to time to see whether on cooling they become crystalline; and when this takes place the evaporation is to be discontinued, the meta-antimoniate of potash then crystallizing abundantly; the alkaline solution is to be poured off, and the salt is to be dried on porcelain plates.

This salt always contains an excess of alkali; it ought to be washed two or three times before it is used as a reagent. As the meta-antimoniate of potash decomposes in solution in water, it should be kept in the dry state, and dissolve when wanted.

To make an examination, which scarcely requires ten minutes, about fifteen grains of the potash to be tried should be dissolved in a small quantity of water and supersaturated with hydrochloric acid, and the solution evaporated to dryness in a porcelain or platina capsule. The chloride of potassium, being then perfectly neutral, is redissolved in water and treated with the solution of meta-antimoniate of potash. If the potash contains 2 or 3 per cent. of soda, a precipitate is almost instantly formed; but if the quantity be smaller, time and agitation will be necessary to effect precipitation.

M. Fremy states the sensibility of this reagent to be so great, that he found by synthetic experiments he could detect half a per cent. of carbonate of soda in commercial potash.—*Ann. de Ch. et de Phys.*, Août 1848.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Identity of Aposepedine with Leucine, and on the true Constitution of these Products. By A. CAHOURS.

PROUST, and subsequently Braconnot, detected amongst the products of the putrefaction of cheese the existence of a crystallizable substance, to which the latter gave the name of *aposepedine*. This substance, which is formed when caseine is exposed to the simultaneous action of water, air and a temperature of 68°–86°, is sometimes obtained in considerable quantity; at other times but mere traces are produced under apparently the same conditions. Some years ago I had commenced an examination of this substance, of which I made some analyses that have not been published, when recently I was led to compare it with leucine. This body has been analysed by Mulder, who has assigned to it the formula $C^{12}H^{12}NO^4$. But this formula is opposed to the ideas of M. Laurent, according to which the sum of the equivalents of hydrogen and nitrogen which enter in the equivalent of a compound must always be divisible by 2. It moreover agrees within 1 equiv. of hydrogen with the formula to which my analysis of aposepedine had led me. I was thus induced to compare these two substances, and I have found them to be perfectly identical in composition, as will be seen by the following results:—

	Aposepedine.			Leucine.		H=1.		
Carbon....	55·19	55·04	54·86	55·12	54·79	12=72		54·96
Hydrogen	9·86	10·11	9·90	10·06	10·04	13	13	9·92
Nitrogen ..	10·63	10·85	..	10·89	..	1	14	10·68
Oxygen ..	..	..	..	..	..	4	32	24·44

These two substances are also identical in their reactions; thus they both enter into combination with nitric and hydrochloric acids, forming beautiful crystalline products. I submitted the first of these compounds to analysis, and obtained numbers leading to the formula $C^{12}H^{13}NO^4, NO^5, HO$.

Leucine exhibits a remarkable composition, for it differs from thialdine, $C^{12}H^{13}NS^4$, in the oxygen being replaced by an equivalent amount of sulphur. The nitrate of thialdine, $C^{12}H^{13}NS^4, NO^5, HO$, has likewise an analogous composition to the nitrate of leucine. It is moreover evident that leucine is a homologue of gly-

cocolle. Admitting the existence of a compound which would be represented by the formula $C^2 H^3 NO^4$, we should obtain, by adding to it $(C^2 H^2)$, $(C^2 H^2)^2$, $(C^2 H^2)^3$, $(C^2 H^2)^4$, $(C^2 H^2)^5$, &c., a series of homologous compounds, comparable to that series of compounds of which formic acid constitutes the first term and cerosic acid the last with which we are yet acquainted. It is then seen that glycocolle, $C^2 H^3 NO^4 (C^2 H^2)$, is the second term of this series, whilst leucine, $C^2 H^3 NO^4 (C^2 H^2)^5$, is the sixth.

On treating leucine with oxidizing agents, or on exposing its solution to the air, it is destroyed, giving off a highly disagreeable odour; at the same time an acid is formed, which is undoubtedly a homologue of glycocollic acid, which should probably be represented by the formula $C^{12} H^{12} O^6$.

Sarcosine, obtained by M. Liebig on treating kreatine with barytic water, and the equivalent of which is represented by the formula $C^6 H^7 NO^4$, is probably another homologue of these products; it is highly probable that under the influence of certain oxidizing agents it may be converted into lactic acid, $C^6 H^6 O^6$.

The preceding results establish most satisfactorily the perfect identity of aposepedine and leucine*. They at the same time show that this remarkable body acts the part of an alkaloid homologous with glycocolle.—*Comptes Rendus*, September 4, 1848.

Examination of the Seed of Peganum Harmala†.

By J. Fritzsche.

On the new Alkaloid Nitroharmalidine and its Salts.

Nitroharmalidine, $C^{27} H^{13} N^3 O^6$.—When harmaline is acted upon by a small quantity of nitric acid, harmine is produced by the removal of 2 equivs. of hydrogen; a larger quantity of this acid deprives the harmaline only of 1 equiv. hydrogen, and its place is taken by the elements of 1 equiv. hyponitric acid. With respect therefore to its amount of hydrogen, nitroharmalidine is situated between harmaline and harmine. According to the views adopted by Berzelius, it belongs to those organic bases which contain a nitrite of an organic oxide conjoined with ammonia. When harmaline is acted upon by nitric acid alone, the nitroharmalidine formed is easily contaminated with harmine and with nitrate of harmaline. A purer product is obtained by treating harmaline with a mixture of sulphuric acid, nitric acid and alcohol (1 part by weight of harmaline, 6–8 parts alcohol of 0·863, then 2 parts concentrated sulphuric acid, and, when the whole is dissolved, 2 parts nitric acid). The mixture is placed in hot water, when very soon the liquid begins to boil violently, owing to the action of the nitric acid upon the alcohol; and when this is continued but for a very short time, the metamorphosis of harmaline into nitroharmalidine is complete; the liquid is cooled as quickly as possible to prevent ulterior decompo-

* Precisely similar conclusions have been arrived at by Messrs. Laurent and Gerhardt.—Ed. *Chem. Gaz.*

† This forms a continuation of the articles inserted at pp. 348, 477 of vol. v. and p. 103 of the present volume.

sition, and the nitroharmalidine separates almost entirely as an acid sulphate in the form of a pale yellow crystalline powder, forming with the dark brown mother-ley a pasty mass. This mass is brought upon a filter, and after the mother-ley has run off, the salt washed with alcohol to which a little sulphuric acid has been added, then dissolved upon the filter in lukewarm water, and the alkaloid precipitated from the solution thus obtained by alkalies.

In general however this solution, even when the process of metamorphosis has been accomplished in a very perfect manner and no formation of harmine has taken place or any harmaline escaped decomposition, nevertheless contains minute quantities of foreign substances, which contaminate the nitroharmalidine on its precipitation by alkalies. To separate these we may proceed in the following manner:—A dilute solution of caustic potash is added in drops to the cold solution, with constant agitation, until a slight permanent precipitate is formed and the colour of the liquid has become pure golden yellow; it is now filtered quickly into a vessel containing a few drops of acid, then heated with this slight excess of acid to between 104° and 122°, and an excess of caustic potash or ammonia added to it at once under constant agitation; this throws down the alkaloid instantly as a beautiful orange-yellow crystalline powder. The addition of acid to the filtered liquid is requisite, because even neutral, and still more so basic solutions of salts of nitroharmalidine experience, when heated or boiled (the latter merely on standing, without any application of heat), a slow decomposition, which gives rise to the formation of a dark-coloured body, which is precipitated by alkalies like an alkaloid. On account of this circumstance, the partial precipitation of the solution must not take place while it is hot, since otherwise, as evident from the change of the golden-yellow colour of the liquid into a darker greenish-yellow, the above decomposition takes place during the filtration. It is advantageous to add the requisite quantity of the precipitant to the prepared solutions at once, because when gradually added the alkaloid generally separates at first in an oily or resinous state, and only becomes solid after some time, and is then not so beautifully crystalline. The temperature of 104°–122° should not be exceeded, because the separation of the alkaloid at a higher temperature does not result instantly but gradually, owing to its tolerable solubility in hot water; and these conditions are favourable for the formation of the above dark-coloured product of decomposition. Much larger crystals are obtained from boiling solutions, but then they always possess a dirty reddish-yellow colour, and leave, on re-solution in cold dilute acetic acid, more or less of the above product of decomposition, with which they are, as it were, intimately penetrated.

Another method of purifying nitroharmalidine from colouring substance consists in precipitating its solution with chloride of sodium or nitrate of soda, and dissolving the muriate or nitrate in cold water on the filter.

Nitroharmalidine can easily be separated from mixtures of harmine and harmalidine by means of sulphurous acid, which forms with it

a sparingly-soluble salt, and with the other two bases readily soluble salts. For this purpose the mixed alkaloids are formed into a uniform paste with a little water, and a saturated solution of sulphurous acid in water added until the smell of the acid remains very predominant; usually the whole dissolves at first; but after some time, dependent on the greater or less amount of nitroharmalidine, the liquid becomes turbid by the formation of a pulverulent yellow precipitate; and the bisulphite of nitroharmalidine gradually separates in this state almost completely, whilst the other two alkaloids continue in solution. When the whole is separated, the salt is collected on a filter, and washed with dilute sulphurous acid from the mother-ley; it is then dissolved in warm water, when usually a small quantity of a brown flocculent substance remains undissolved; and the filtered solution is either precipitated immediately by an excess of alkali, or submitted, if necessary, to the above process of purification.

The nitroharmalidine obtained from aqueous solutions frequently forms microscopic crystals; from alcoholic solutions it may be obtained in larger crystals. It is but sparingly soluble in cold water, colours it however yellowish; it dissolves in much larger quantity in boiling water; and as it separates from this solution on cooling in well-formed crystals, which are perceptible to the naked eye, it can in certain cases be purified in this manner. On precipitating solutions of its salts by alkalies, a pretty considerable quantity remains in solution, as is also the case with harmaline and harmine; it cannot be obtained in an unaltered state by evaporating the more or less yellow-coloured liquid.

Nitroharmalidine dissolves in alcohol far more readily than harmaline or harmine, and imparts an intense yellow colour to it; it is still far more soluble when heated, and crystallizes from this solution on cooling in dark orange-yellow crystals. It is but sparingly soluble in æther at the ordinary temperature, and separates in minute crystals on evaporating the light yellow solution; boiling æther dissolves it more readily, without however depositing crystals on cooling. An alcoholic solution of the alkaloid, prepared without the assistance of heat, is not precipitated by æther. Essential oils take up a considerable quantity of nitroharmalidine at a high temperature, and deposit it again on cooling; olive oil acts in the same manner.

Nitroharmalidine expels the ammonia from ammoniacal salts on boiling, and takes its place; but as the conditions requisite for the above-mentioned metamorphosis occur, this usually takes place to a greater or less extent. The alkaloid dissolves abundantly in a solution of chloride of ammonium, even before boiling, and separates on cooling in a crystalline state. With acids it forms yellow salts.

Nitroharmalidine furnished on analysis the following results:—

Carbon.....	60·37	61·84	61·02	61·54	27	= 2028·24	61·17
Hydrogen ..	5·01	5·22	5·19	5·14	13	162·14	4·89
Nitrogen	14·61	14·95	16·24	..	3	525·18	15·84
Oxygen	..	..	..	..	6	600·00	18·10

According to Berzelius's view, nitroharmalidine must be looked

upon as a nitrite of an organic oxide conjoined with ammonia, and its composition would be expressed by the following rational formula:—$(C^{27} H^{10} NO^3 + NO^3) + NH^3$. The conjunct might be called the nitrite of the oxide of harmalidene. The symbol for the alkaloid would be n i h l d Ak, according to Berzelius's new mode of notation.

Muriate of Nitroharmalidine, $C^{27} H^{13} N^3 O^6 + HCl$, forms minute yellow prisms when the base is mixed with alcohol, a large excess of muriatic acid added, and the solution rendered complete by heat, and allowed to cool. It may also be obtained from the watery solution of the acetate by precipitation with excess of muriatic acid; and, finally, it is also precipitated almost wholly by chloride of sodium from solutions of the alkaloid in acids, like the corresponding salts of harmaline and harmine. On analysis it furnished—

Nitroharmalidine	..	..	87·11	1	=3315·66	87·92
Muriatic acid.....	12·22	12·14	12·06	1	455·76	12·08

Nitroharmalidine and Chloride of Platinum, $PtCl^2, C^{27} H^{13} N^3 O^6$, HCl, falls, on mixing a solution of the muriate of nitroharmalidine with one of chloride of platinum, as a yellow flocculent precipitate, which however soon becomes darker and crystalline. It gave on analysis—

Carbon	34·38	34·04	..	27	=2028·24	34·435
Hydrogen	3·04	3·12	..	14	174·72	2·966
Nitrogen	..	..	..	3	525·18	8·916
Oxygen	..	..	..	6	600·00	10·187
Chlorine.....	..	..	..	3	1329·84	22·578
Platinum	..	..	21·09	1	1232·08	20·918

The Perchloride of Mercury forms with the muriate of harmalidine a double salt, which separates as a pale yellow flocculent precipitate, that soon becomes crystalline. It falls in larger crystals from hot solutions on cooling.

The Hydrobromate and Hydriodate of Nitroharmalidine are obtained by precipitating a solution of the acetate with solutions of an alkaline bromide or iodide, when these salts separate in crystals which resemble those of the muriate.

Hydrocyanate of Nitroharmalidine appears not to exist in a separate state, nitroharmalidine forming, like harmaline, a peculiar compound when mixed with hydrocyanic acid. But it exists in combination with the proto- and percyanide of iron, forming with them very sparingly double salts. The protocyanide separates, after a short time, on mixing a solution of ferrocyanide of potassium with one of a salt of nitroharmalidine, in very minute light brown crystals in feathery groups. The persalt is obtained in the same manner, on employing the ferridcyanide of potassium, as a yellow crystalline powder; but this salt separates in the first moment in oily drops, imparting a milky appearance to the liquid, and assumes a crystalline form only after some minutes.

Sulphocyanide of Nitroharmalidine is a pale yellow, rather spa-

ringly soluble salt, which separates in microscopic needles on mixing solutions of nitroharmalidine and sulphocyanide of potassium.

Sulphate of Nitroharmalidine. 1. *Neutral Salt.*—This is gradually precipitated in a crystalline state from a solution of the neutral acetate in which sulphate of ammonia is dissolved to saturation; but as it is tolerably soluble in water, it is difficult to obtain it pure in this manner. To obtain it in a direct manner, dilute sulphuric acid must be digested with an excess of the alkaloid in the cold, and the filtered solution evaporated at the ordinary temperature; no heat must be employed, as the liquid would soon begin to experience the metamorphosis above described, and which is indicated by its colour at first becoming darker, and then passing gradually into green.

2. The *Acid Salt* is obtained when the alkaloid is dissolved in boiling alcohol which has been mixed with a large excess of sulphuric acid, filtering the solution if necessary, and then allowing to cool, when the salt separates in pale yellow crystals. It is also obtained when the alkaloid is dissolved in an excess of concentrated sulphuric acid, and the dark brownish red solution dropped very gradually into cold water, with constant agitation, when the salt soon separates as a crystalline powder, which being but sparingly soluble in cold water, may be separated by washing from adherent excess of acid. A sample, prepared from alcohol in the manner above described, gave on analysis the following results:—

Nitroharmalidine	72·77	1 =	3315·66	72·998
Sulphuric acid	21·98	2	1001·50	22·049
Water		2	224·96	4·953

Sulphite of Nitroharmalidine.—Recently-precipitated nitroharmalidine dissolves in aqueous sulphurous acid, but soon separates as a sparingly-soluble acid salt, which is now scarcely soluble in cold water, and still less in water saturated with sulphurous acid.

Nitrate of Nitroharmalidine separates from the hot solution on cooling in yellow crystalline needles. It is sparingly soluble in pure water, and still more so in water containing nitric acid. It may also be obtained from a solution of the acetate by the addition of nitric acid or nitrates.

Carbonate of Nitroharmalidine exists merely in solutions which are obtained by digesting the alkaloid with carbonic acid water. Bicarbonate of potash precipitates from solutions of salts of nitroharmalidine as beautiful a crystalline substance in the cold as caustic alkalies at high temperatures; the composition of this precipitate could however not be ascertained with sufficient certainty; it appears to be chiefly pure alkaloid, but it is evident that some carbonate is mixed with it, from the circumstance that on washing it for some length of time a liquid is obtained which yields with alkalies a pretty considerable precipitate of nitroharmalidine.

Oxalate of Nitroharmalidine.—Nitroharmalidine is very readily soluble in oxalic acid, and is not precipitated by the addition of an excess of oxalic acid to this solution. It can be obtained on evaporation in a crystalline form.

Acetate of Nitroharmalidine.—Nitroharmalidine is easily soluble in acetic acid; and on evaporating this solution at the ordinary temperature, the acetate is obtained in a crystalline state.

Chromate of Nitroharmalidine.—The alkaloid forms with chromic acid an acid salt, which first separates in oily drops on mixing the solutions, but soon crystallizes. This salt is nearly insoluble in cold water, but dissolves rather easily in boiling water and in alcohol without decomposition, and separates unaltered on cooling. Like the chromates of harmaline and harmine, this salt also experiences when heated a sudden decomposition, which in general is accompanied by the phænomena previously described under those salts; it is, however, much more violent.—*Bulletin de St. Pétersb.*, vii. p. 129.

On the Cinnabar Mines of Upper California.
By the Rev. C. S. Lyman.

The mine of New Almaden is situated a few miles from the coast, about midway between San Francisco and Monterey, and in one of the ridges of Sierra Azul mountain. The mouth of the mine is a few yards down from the summit of the highest hill that has yet been found to contain quicksilver, and is about 1200 feet above the neighbouring plain, and not much more above the ocean. This hill extends longitudinally in a north-westerly direction, decreasing in height; and in various parts of it, for several miles, traces of the ore have been found, and some openings have been made which promise to be valuable. This range of hills consists of a variety of rocks, which I have not yet had an opportunity properly to study. The prevailing one is a greenish talcose rock, which seems to embrace the bed of ore at the New Almaden mine both above and below. A specimen from the rock immediately contiguous to the ore is contained in the box. The ore is interspersed through a yellow ochreous matrix, which forms a bed 42 feet in thickness, dipping north-westerly at an angle of about 45°. The richest ore is at present found in the upper part of the bed, the poorer ores being taken from the lower portion.

This mine, known to the aborigines from time immemorial as a "cave of red earth," from which they obtained paint for their bodies, was first discovered to contain quicksilver about four years since, during experiments made by some Mexicans to smelt the ore for the purpose of obtaining *gold*, which they supposed it to contain. About two years ago it fell into the hands of Barron, Forbes and Co., who sent on hands, tools and funds to commence working it. Unfortunately the vessel fell into the hands of the United States forces, and was confiscated; the operations of the mine were of course delayed till the arrival of Mr. Forbes himself a few months since, with miners, tools, and whatever things he was able to procure in Mexico, to enable him to make a fair experiment on the capabilities of the mine. The great trouble was to obtain suitable apparatus for extracting the ore. At length four potash kettles were found, which were set in a furnace of adobies, with condensers of mason-work

immediately adjacent—a wretched apparatus indeed for managing so subtle a thing as mercurial vapour. While I was at the mine the daily mode of working was to fill these pots in the morning with 1600 lbs. (400 to each pot) of the ores of average quality, broken in lumps of the size of apples, put on the covers and *lute* them with a layer of *sand*. The fires were then kept up till near night, when the furnaces were allowed to cool gradually. The next morning the condensers were opened, and the metal dipped up; which usually amounted to from 200 to 300 lbs. for the four pots. This was a much less per-centage than the assay indicated, and it was obvious that a large portion of metal was lost. The upper parts of the pots and condensers were found to be generally coated with a crust of sulphuret of mercury, of which No. 15 is a small specimen. Mr. Forbes wished to devise some way of extracting the metal without mixing lime with the ore in the roasting, but was unsuccessful. At length a kiln of lime, which occurs in the immediate vicinity, was burned; and I am informed that, mingled with this, the ores yield a vastly larger per-centage of metal. In the last three weeks about 10,000 lbs. of metal have been extracted with the same apparatus, being a yield of over 50 per cent. Whether the ores were picked or not I cannot say, but presume they were. Between 15,000 and 20,000 lbs. have been extracted in about two months, only six miners having been employed in digging the ore, and the hands of the establishment, all told, miners, furnace-men, wood-choppers, &c. &c., numbering only a score. The mine is probably yielding a net profit of 100,000 dollars a year with its present crude apparatus. With suitable furnaces and iron cylinders or retorts, the mine would easily yield 1,000,000 dollars and upwards. Mr. Forbes sails to Europe shortly for the apparatus necessary. The bed has as yet been followed but a few hundred feet, but the ores grow more and more rich and abundant.

The other mines opened in the vicinity have not yet been sufficiently developed to decide upon their character. Ore has been found in fifteen or twenty other places within a few miles around, and within a few days in hills that do not seem to belong to the same range with that which contains the mine already described.

Some ores of silver have also been recently discovered in this region; but I have had no opportunity of procuring any genuine specimens as yet, and whether silver mines worth the working will be found is at least problematical.

There are traces of coal in the country, but nothing of value has yet been discovered.

Gold has been found recently on the Sacramento, near Sutter's Fort. It occurs in small masses in the sands of a new mill-race, and is said to promise well.—Silliman's *Journal*, September 1848.

On the Cyanic Æthers and their Derivatives. By A. Wurtz.

Cyanic æther is formed with cyanuric æther when cyanate of potash is distilled with the sulphovinate of the same base. The two

æthers are easily separated by distillation, the first being extremely volatile, while the latter boils only at a very high temperature.

The cyanic æther, when purified by several rectifications over chloride of calcium, forms a very mobile and highly refractive liquid; its odour is extremely irritating, and causes a flow of tears. It is lighter than water, and the density of its vapour was found to be 2·4. Its composition is expressed by the formula $C^6 H^5 NO^2 = C^2 NO, C^4 H^5 O = 4$ vols. of vapour.

When cyanic æther is treated with a solution of ammonia, it dissolves in it with disengagement of heat; and on evaporation of the liquid a compound is obtained which crystallizes in beautiful prisms. The composition of this substance, expressed by the formula $C^6 H^8 N^2 O^2$, shows that the elements of ammonia have been simply added to those of the cyanic æther without any elimination of water. The crystals are fusible, and very soluble in water and in alcohol; they disengage ammonia when boiled with potash. Cyanic æther experiences a very remarkable modification under the influence of water, resembling in a certain degree the reactions exhibited by cyanic acid itself; carbonic acid is disengaged, and the æther is converted into a crystalline mass, which it is easy to purify by solution in water or in alcohol. The composition of this new substance is represented by the formula $C^{10} H^{12} N^2 O^2$; and the reaction which gives rise to it may easily be explained by the following equation:—

$$2C^6 H^5 NO^2 + H^2 O^2 = C^2 O^4 + C^{10} H^{12} N^2 O^2.$$

The Cyanate of Methyle, $C^4 H^3 NO^2 = C^2 NO, C^2 H^3 O$, is obtained by distilling cyanate of potash with an alkaline sulphomethylate; it is a very volatile liquid, which is separated with the greatest ease from the cyanurate of methylene, which is far less volatile and is formed at the same time. Like cyanic æther it dissolves in ammonia, and gives rise to a crystalline compound with the formula $C^4 H^6 N^2 O^2$. Water instantly decomposes it into carbonic acid and a solid crystalline substance, which is isomeric with the ammoniacal cyanic æther. This last reaction is expressed by the following formula:—

$$2C^4 H^2 NO^2 + H^2 O^2 = C^2 O^4 + C^6 H^8 N^2 O^2.$$

From what precedes, it is seen that cyanic æther and the cyanate of methylene give rise to substances whose composition approaches in a certain degree that of urea. Let us imagine, in fact, that the elements of 1 equiv. of methyle, $C^2 H^2$, are added to the elements of urea, the substance $C^4 H^6 N^2 O^2$, corresponding to the urea in the acetic series, will result from this combination; it will be, in the expressive language of M. Gerhardt, a homologue of that substance. The crystals which I have obtained by treating the cyanate of methylene with ammonia are nothing less. If to this latter compound we again add the elements of 1 equiv. of methylene, we rise one degree in the scale and obtain the substance $C^6 H^8 N^2 O^2$, the homologue of urea in the metacetic series. This substance exists, and may be obtained in two different ways—either by treating cyanic æther with ammonia, or by decomposing the cyanate of methylene

by water. Lastly, the compound $C^{10} H^{12} N^2 O^2$, obtained by treating cyanic æther with water, constitutes the homologue of urea in the valerianic series.

It will be seen that, as regards their general composition, the substances derived from the cyanic æthers constitute a series which it will be easy to increase by two new terms on isolating the cyanate of amylene. It must however be observed, that if these substances are viewed with reference to their constitution and chemical functions, it appears doubtful whether the analogy which the empirical formulæ indicate is maintained. From the experiments which I have hitherto made, the compounds obtained, the one by treating cyanic æther with ammonia, the other by decomposing cyanate of methylene with water, are not identical, but simply isomeric. This implies a difference in the constitution and in the chemical reactions of these two bodies. I might venture to state that the first is related to urea, whilst the second should be arranged amongst those bodies which have been termed *amethanes*, and which may be regarded as æthers in intimate combination with amides. The formula $C^4 H^6 N^2 O^2$ may, in fact, be divided in the two following ways:—

$$C^6 H^8 N^2 O^2 = C^2 NO, C^4 H^5 O, NH^3 = C^2 NO, C^2 H^3 O + C^2 H^3 (NH^2).$$

The first of these rational formulæ is that of urea, in which 1 equiv. of water is replaced by an equivalent of æther; the second indicates a combination of cyanate of methylene with methylamide, that is to say, methylic æther, $C^2 H^3 O$, in which the molecule of oxygen is replaced by a molecule of amidogen, NH^2. On applying this hypothesis to the substance $C^{10} H^{12} N^2 O^2$, it may be regarded as cyanic æther combined with ætheramide, as will be evident from the following equation:—

$$C^{10} H^{12} N^2 O^2 = C^2 NO, C^4 H^5 O + C^4 H^5 (NH^2).$$

Comptes Rendus, August 28, 1848.

On the mutual Decomposition of some Haloid Salts.
By Prof. G. L. Cantu.

It is well known to chemists that chlorine decomposes hydrobromic and hydriodic acids, as well as metallic bromides and iodides; also that bromine decomposes hydriodic acid and the iodides, in the former case the chlorine taking the place of the bromine and iodine, and in the latter the bromine replacing the iodine, in each instance the less electro-negative element being set free. No chemist however has, to my knowledge, turned his attention to the action that the chlorides exert on bromides, and these latter on iodides, the latter element being combined with a more electro-positive metal than that preceding it, when they are brought to react on one another at a temperature sufficiently elevated to cause their fusion. Although it was possible, reasoning on the principles of the electro-chemical theory, to foresee in some measure the results of such a reaction, it was nevertheless to be desired that experiment should demonstrate that which might reasonably be supposed was

indeed the case before such results could be received as established facts.

The fact is, that when chloride and bromide of potassium are exposed together, out of contact of air, to a temperature sufficient to cause their fusion, the only effect is an intimate mixture of the two salts without decomposition. The same occurs when the chloride or bromide of potassium is fused with the iodide of the same metal. But very different is the effect when a chloride is brought to act on a bromide or iodide having for base a metal more electro-positive than that combined with the chlorine. Then the chlorine combines with the base of the latter, expelling the bromine or iodine, which combine totally or in part with the less electro-positive metallic base abandoned by the chlorine, and an exchange of bases, so to speak, takes place; a portion, however, more or less notable, of the bromine, or more especially of the iodine, is set free when the metal abandoned by the chlorine has a weak affinity for the other element, which is the case with the metals of the earths, and more particularly with substances exercising a weaker affinity than these. From these results, which accord so well with the electro-chemical theory, I was naturally led to believe that the fluorides, whose halogenous element is so eminently electro-negative in relation to chlorine, bromine, and particularly iodine, would necessarily behave in like manner towards the haloid salts formed by these elements, when the metallic base was more electro-positive than that combined with the fluorine. And on bringing fluoride of calcium to react on chloride of sodium or potassium at a heat sufficient to cause its fusion, their mutual decomposition took place, producing chloride of calcium and fluoride of sodium or potassium. The same takes place with fluoride of calcium and iodide of potassium, with this difference however, that a great part of the iodine goes off in the state of vapour, owing to the weak affinity of the iodine for the calcium being overcome by the repulsive force of the caloric; so that it may be considered as established generally, that a fluoride decomposes an iodide, a bromide or a chloride when the latter is combined with a metallic base more electro-positive than that of the fluoride on which it is brought to react. The same holds with regard to a chloride in relation to a bromide or iodide, to a bromide in relation to an iodide.

From these results it appears to me that the following corollaries may be deduced:—

I. In the calcination of all substances, organic or inorganic, in which these haloid salts exist under the conditions described, an alteration, more or less sensible, in the natural state of the compounds contained in it, must take place with a notable loss of bromine, and more especially of iodine, and probably even of some portion of the chlorine.

II. To diminish as much as possible such alteration and loss, it is necessary to conduct the calcination in a close vessel, and at the lowest heat capable of producing the effect.

III. In searching for bromine or iodine in mineral waters, or other substances in which the conditions above-mentioned may exist,

it is advisable to add pure carbonate of potash, with which these two elements may combine, and become more fixed.

IV. Certain fluorides may be employed advantageously in the detection of iodine, and among them the fluoride of aluminum should be particularly mentioned; and I have already used it for this purpose with great success.—*Raccolta Fisico-Chimica Italiana*, No. xxviii. 1848.

On the Modifications which Tartaric and Paratartaric Acids experience by Heat. By MM. LAURENT *and* GERHARDT.

According to M. Fremy, tartaric acid passes through two intermediate stages before losing the whole of its constitutional water by the action of heat in order to become anhydrous, and forms two acids differing from tartaric acid in their capacity of saturation. We have found that *tartaric acid may become modified without experiencing any loss, and consequently without any change in composition.* If we take, for instance, a known weight, say 1 grm., of tartaric acid, and heat it carefully, so as to cause it to fuse, but not above this point, the acid will be modified, and will not have lost one-thousandth in weight. The product is a mixture of two acids isomeric with tartaric acid. One of them, confounded by M. Fremy with unaltered tartaric acid, possesses the same capacity of saturation; we have called it *metatartaric acid.* This, like tartaric acid, furnishes crystallizable salts, which are distinguished from the corresponding tartrates by their form and their greater solubility; the bisalts of ammonia, $C^4 H^5 AmO^6$, and the neutral salts of lime, $C^4 H^4 Ca^2 O^6 + 4Aq$*, being especially characteristic in this respect. As far as it is possible to ascertain with the microscope, the metatartrate of lime appears to be hemihedral; it is probable therefore that metatartaric acid and the metatartrates will act upon polarized light like tartaric acid and the tartrates. Moreover, they are converted into the latter by ebullition.

The other isomeric acid, which we have named *isotartaric*, is produced to a greater or less amount according to the duration of the fusion of the tartaric acid. It is remarkable from its neutral salts possessing the composition of the bitartrates. Thus in this modification the tartaric acid has changed its capacity of saturation, without any alteration of composition, but by the sole effect of a molecular transposition.

When the solution of the neutral isotartrate of lime, $C^4 H^5 CaO^6$, an extremely soluble and uncrystallizable salt, is heated, it becomes acid, and is converted into neutral crystallizable metatartrate of lime and metatartaric acid. In the same manner the solution of the isotartrate of ammonia is converted by heat into bimetatartrate of ammonia without any ammonia being set free, the two salts being isomeric. It is curious to see this retrocession into tartrates of the isomeric molecules of the isotartrates and metatartrates under the

* In this paper M. Gerhardt's notation has been retained, $C^4 H^4 Ca^2 O^6 + 4Aq = C^8 H^4 O^{10}, 2CaO + 8Aq$.

influence of heat, that is to say, of the same agent which produced them, only applied under other circumstances.

If, instead of merely melting the tartaric acid, it is heated as long as any water is disengaged, and so as to cause it to puff up, it is converted into a third acid, containing all the elements of tartaric acid less 1 equiv. of water, $C^4 H^4 O^5$. This acid, which is very soluble in water, and even deliquescent, furnishes salts, the composition of which is represented by that of the bitartrates less 1 equiv. of water. It is evidently the acid of which M. Braconnot has described the characters, and which M. Fremy has named *tartrelic*. Its reactions are peculiar; the insolubility of its lime salt, $C^4 H^3 CaO^5$, is such that it produces a milkiness in acetate of lime, even when the solution is so dilute as not to be rendered turbid by the metatartrates, nor even by the tartrates; the turbidness does not disappear on the addition of ammonia. But when the acid is first saturated with ammonia, the acetate of lime no longer causes a precipitate, even when the solution is highly concentrated, because ammonia, as well as potash, instantly converts M. Braconnot's acid into isotartrate, the lime salt of which is very soluble. We have founded upon this reaction a very easy method of obtaining the isotartrates in a pure state. This experiment is interesting, as it shows the retention of the capacity of saturation of an acid notwithstanding the assimilation of the elements of water, and of that very acid which has precisely the composition of the pretended anhydrous tartaric acid, so that with the dualistic theory we arrive at this result, that anhydrous tartaric acid is both an anhydrous and a hydrated acid. Is not this a decided proof of the error of the dualistic doctrines, when they attribute to what is called the water of hydration the determining cause of the capacity of saturation of acids?

According to M. Fremy, his soluble tartrelic acid by losing more water is converted into an insoluble anhydrous acid. This metamorphosis however is only another case of isomorphism, which we have positively ascertained by means of the balance.

We may add, that paratartaric acid has furnished us with a series of modifications similar to those of tartaric acid.—*Comptes Rendus*, September 25, 1848.

On the Isomorphism of the Nitrite of Lead with the Nitrate. *By* J. Nicklès.

The nitrite of lead is capable of crystallizing in every proportion with the nitrate; moreover its crystalline form is identical with that of the latter; it is a regular octahedron. The identity of form and the property of crystallizing together constitute therefore a case of isomorphism. Hitherto the nitrite of lead has been considered to be anhydrous, whence certain authors have pointed out this case of isomorphism as being contrary to the law of M. Mitscherlich. They view the isomorphism of the nitrite of lead with the nitrate as an anomaly.

On analysing some crystals of nitrite of lead, well-dried between

blotting-paper, they yielded 5·87 and 5·82 per cent. of water, which does not differ considerably from the theoretical number, 5·47. The atom of nitrate of lead, $NO^4 + O$, PbO, consequently becomes in the nitrite $NO^4 + H$, PbO.—*Comptes Rendus*, August 28, 1848.

A new Method of extracting pure Gold from Alloys and from Ores. By C. T. Jackson.

The following method of obtaining pure metallic gold in the form of a spongy mass has been practised by me for several years, and no account of the process has, to my knowledge, heretofore been published. It is very useful to the chemist and to the manufacturer, and is more œconomical than any other method that I am acquainted with.

After separating the gold from silver by means of a mixture of nitric and hydrochloric acids, as is usually done, the solution containing gold and copper is to be evaporated to small bulk, and the excess of nitric acid is thus driven off.

A little oxalic acid is added, and then a solution of carbonate of potash sufficient to take up nearly all the gold in the state of aurite of potash is gradually added. A large quantity of crystallized oxalic acid is now added, so as to be in great excess, and the whole is to be quickly boiled. All the gold is immediately precipitated in the form of a beautiful yellow sponge, which is absolutely pure metallic gold. All the copper is taken up by the excess of oxalic acid, and may be washed out.

Boil the sponge in pure water so long as any trace of acidity remains, and the gold is then to be removed from the capsule and dried on filtering-paper. It may be formed into rolls, bars or thin sheets, by pressing it moderately in paper. I have made several useful applications of the gold sponge thus prepared, and had a tooth plugged with it in October 1846, to which purpose it is well-adapted.

By moderate pressure the spongy gold becomes a solid mass, and burnishes quite brilliantly.

The jeweller or goldsmith will find spongy gold to be quite convenient when he requires it for a solder, and it is a convenient form of the metal for making an amalgam for fine gilding. I have used it for some years in soldering platina, and prefer it to the filings or gold foil for that purpose. This method of separating fine gold from coarse is very simple, and cheaper than the usual processes. It is applicable in the separation of gold from ores that may be treated by acids, and is vastly preferable to the method commonly used by chemists and assayers.

When making oxide of gold for dentist's use, the chemist will find that oxalic acid added to his potassic solution will at once recover all the gold that is dissolved in an excess of the alkaline solution*. Many other applications of this very simple method will occur to chemists and artisans.—Silliman's *Journal*, September 1848.

* Much gold is lost by the usual method of preparing the oxide.

ANALYTICAL CHEMISTRY.

On the Application of Chloride of Ammonium in Analytical Chemistry. By Prof. H. Rose.

Prof. Rose recently drew attention* to the very great use that might be made of the chloride of ammonium in quantitative analysis, from its converting several metallic oxides, when heated with them, into chlorides; the more volatile chlorides escape, and can thus be separated from the less volatile. Not merely oxides, but likewise several sulphurets are converted by chloride of ammonium into chlorides; for instance, the sulphurets of antimony, arsenic, tellurium and tin. The following additional observations respecting the behaviour of various bodies towards chloride of ammonium have been since published:—

Titanates.—When titanic acid is calcined with chloride of ammonium, the ammoniacal salt is driven off, and the titanic acid does not decrease in weight.

Titanic acid forms with the alkalies only acid insoluble salts; they dissolve in hydrochloric acid, except when deprived of their water by a red heat; they are then perfectly insoluble. It is consequently very difficult to ascertain their composition, especially when it is desired not to determine their amount of water by the loss. However this is very easily accomplished by treating them with chloride of ammonium. The amount of water is first determined by ignition, the calcined compound mixed with sal-ammoniac, the mixture heated to redness, and this operation repeated until no further increase in weight results. While the titanic acid continues unaltered, the alkali exchanges its oxygen for chlorine, and the entire composition of the anhydrous salt can therefore be calculated merely from the increase in weight, for the difference between the atomic weight of the oxygen and chlorine is to the atomic weight of chlorine as the increase in weight to the amount of chlorine in the mass treated with sal-ammoniac; but from this amount of chlorine that of the alkaline metal can be obtained, and also that of the titanic acid.

This determination can be checked in a very simple manner by treating the mass calcined with chloride of ammonium with water, which dissolves the alkaline chloride, the amount of which can be determined by evaporation, while the titanic acid remains undissolved.

It resulted from the experiments made on this subject, that the potash salt dried at 212° has the formula $KO,6TiO^2 + 3HO$, and the soda salt $2NaO,9TiO^2 + 5HO$. The first forms a powder, which appears perfectly crystalline under the microscope; the latter is not at all crystalline under the microscope, and consists of vitreous fragments.

Sulphates.—The alkaline sulphates are completely decomposed on ignition with chloride of ammonium into alkaline chlorides, from the weight of which the amount of the sulphate can be accurately estimated. Sulphate of baryta is likewise decomposed by chloride

* Chem. Gaz., p. 166 of the present volume.

of ammonium; but it is almost impossible to render the decomposition complete, because the chloride of barium formed melts, and so protects the undecomposed sulphate of baryta from further decomposition. Sulphate of magnesia is not decomposed by chloride of ammonium.

Seleniates.—Seleniate of baryta is converted, on calcination with chloride of ammonium, into a mixture of selenite of baryta and chloride of barium, which is coloured brown by free selenium.

Alumina Compounds.—Calcined alumina, rubbed to a fine powder, is for the greater part volatilized by treatment with sal-ammoniac. A small portion, however, of coarser nature, most tenaciously resists the action of the chloride of ammonium; and the alumina finally acquires, by the long ignition, such a state of density that it cannot be further decomposed by chloride of ammonium. Sulphate of alumina, calcined with chloride of ammonium, is volatilized without leaving a residue.

Potash alum is completely decomposed; however, it does not leave pure chloride of potassium, but the sparingly volatile double compound of chloride of aluminum and chloride of potassium.

Glucina.—The compounds of this earth closely resemble those of alumina in their behaviour towards chloride of ammonium. The loose carbonate of glucina is more quickly decomposed by chloride of ammonium than the earth precipitated by ammonia; but even the former cannot be entirely volatilized by frequent treatment with chloride of ammonium. The more frequently the earth is heated to redness, the more it resists further decomposition.

Peroxide of Iron.—When mixed with chloride of ammonium and heated to redness, the mixture fuses, and readily flows over the crucible. A considerable quantity of iron is volatilized in red vapours as perchloride; and on the sides of the crucible peroxide of iron is deposited in a crystalline state, produced from the chloride by oxidation.

Manganese.—The oxides of this metal are converted, by treatment with chloride of ammonium, into protochloride, in which by oxidation some protoperoxide is formed.

Oxide of Nickel and Cobalt are converted into the metallic state when calcined with chloride of ammonium. The arseniuret of nickel (*Nickelspeise*) is, on the contrary, only partially decomposed, the arsenic being volatilized and the nickel left as chloride.

Oxide of Bismuth is reduced, with a lively deflagration, to metallic bismuth.

Silver Compounds.—Chloride of silver, mixed with chloride of ammonium and calcined, experiences no change; oxide of silver, heated to redness with chloride of ammonium, leaves both metallic silver and chloride. By the first action of the heat a portion of the oxide is reduced to metallic silver, which is not altered by ignition with sal-ammoniac; that portion of the oxide which has not been reduced by the heat before the chloride of ammonium begins to act is converted into chloride of silver. Antimoniuret of silver (the native coarse-grained mineral from Wolfach, Ag^2Sb) is but imper-

fectly decomposed by chloride of ammonium; by repeated treatment it is most probable that metallic silver would remain, since the more frequently it is calcined with chloride of ammonium, the more the antimoniuret of silver decreases in weight, and the residue becomes less brittle.

Lead Compounds.—Oxide of lead, calcined with chloride of ammonium, is converted into chloride of lead, which, on the access of air and the repeated addition of chloride of ammonium, may be entirely volatilized. Sulphuret of lead, calcined with sal-ammoniac, gives a fused blackish-brown residue, which is a compound of chloride and sulphuret of lead, and which, on the access of air, gives off dense vapours of chloride of lead, and may be wholly volatilized by the repeated addition of sal-ammoniac.

Oxide of Zinc is entirely volatilized as chloride of zinc when mixed with chloride of ammonium, but with great difficulty when the air is excluded.

Sulphate of zinc, deprived of its water of crystallization and calcined with chloride of ammonium, froths up very considerably. By repeated treatment with chloride of ammonium the residue can be wholly volatilized.

Oxide of Chromium and Chromates.—The first experiences no change by calcination with chloride of ammonium, but the alkaline chromates leave a mixture of oxide of chromium and alkaline chloride; the latter dissolves on treatment with water, while the former is left undissolved. The alkaline chromates may be easily and accurately analysed by this method. The double sulphate of potash and oxide of chromium, after being deprived of its water, is converted into a mixture of oxide of chromium and chloride of potassium on ignition with sal-ammoniac.

Silicic Acid.—Silicic acid, which has not been heated too strongly, decreases somewhat in weight on treatment with chloride of ammonium; but by long ignition it attains such a state of density as to withstand the action of sal-ammoniac. Crystallized silicate of soda in the anhydrous state is barely decomposed by ignition with chloride of ammonium.

Phosphates.—Phosphate of soda, calcined with chloride of ammonium, increases in weight; however, the weight of the residue diminishes by further treatment with sal-ammoniac, but still remains greater than that of the phosphate employed. A partial decomposition takes place; chloride of sodium is formed, and some phosphoric acid is expelled in the state of chloride. But if the heat is continued longer after the chloride of ammonium is volatilized, chlorine is expelled as hydrochloric acid by the phosphoric acid under the influence of the air and moisture, whence the alternating increase and decrease in weight. Phosphate of lime is not decomposed by ignition with sal-ammoniac.

Compounds of Antimony.—The author has already shown that the antimony can be entirely expelled from the alkaline antimoniates by chloride of ammonium, and the alkali determined with accuracy

as chloride. The combinations of the alkaline sulphurets, especially the sulphosalt, consisting of sulphuret of sodium and sulphuret of antimony, commonly known by the name of Schlippe's salt, may be exceedingly well analysed by chloride of ammonium. In the case of this salt, pure chloride of sodium was left entirely free from every trace of antimony and sulphur.

Arseniates.—That the alkaline arseniates are most readily converted by chloride of ammonium into alkaline chlorides has been already shown. The arseniate of lime, after calcination, leaves chloride of calcium, but the arseniate of magnesia is scarcely affected by treatment with sal-ammoniac. Sulphate of ammonia appears to decompose it entirely; however, this ammoniacal salt is not so well adapted for analytical purposes, as it fuses when heated and froths violently, rendering it difficult to prevent the mass flowing over the crucible.

Borates.—Borax is not affected by calcination with sal-ammoniac; the latter escapes on the application of heat before the borax begins to fuse.

Fluorides.—Fluoride of sodium is decomposed by calcination with chloride of ammonium; it is however with great difficulty. The layer of fused chloride of sodium protects the still-undecomposed fluoride from further decomposition by chloride of ammonium. Fluoride of calcium is still less easily decomposed.

Bromides.—Bromide of sodium is decomposed, but not completely, by calcination with chloride of ammonium. When the treatment is frequently repeated, the residue consists principally of chloride of sodium, but always contains a considerable amount of bromide.

Iodides.—Iodide of potassium is decomposed by ignition with chloride of ammonium; but it is not entirely converted into chloride of potassium, even when the treatment is frequently repeated.

It is remarkable, that not only is chloride of ammonium incapable of decomposing the bromides and iodides completely, but also that it behaves exactly in the same manner towards fluorides, the partial decomposition of which by chloride of ammonium was not to be expected.

Nitrates.—Nitrate of potash is easily and entirely decomposed by chloride of ammonium, and yields accurately the amount of chloride of potassium corresponding to the salt.—*Proc. of Berlin Academy*, May 1848.

Mode of detecting Alcohol in Chloroform. By M. Cattel.

The author adds one or two crystals of chromic acid to 2 drms. of the suspected chloroform; when alcohol is present the chromic acid is soon reduced to green oxide. The same result is obtained by adding a little bichromate of potash and sulphuric acid instead of the chromic acid.—*Journ. de Chim. Méd.*, iv. p. 257.

CHEMICAL PREPARATIONS.

Preparation of Collodion, or Solution of Gun-Cotton, as an Adhesive Material for Surgical Purposes.

M. Malgaigne has recently communicated to the French Medical Journals some remarks on the preparation of gun-cotton for surgical purposes. Several French chemists, at the suggestion of M. Malgaigne, attempted to make an ætherial solution of this compound by pursuing the process recommended by Mr. Maynard in the 'American Journal of Medical Sciences,' but they failed in procuring the cotton in a state in which it could be dissolved by æther. It appears that these experimentalists had employed a mixture of nitric and sulphuric acids; but M. Mialhe ascertained, after many trials, that the collodion, in a state fitted for solution, was much more easily procured by using a mixture of nitrate of potash and sulphuric acid.

For the information of our readers who may be disposed to try this new adhesive material, we here give a description of M. Mialhe's process for its preparation. It appears, from the results obtained by this chemist, that cotton, in its most explosive form, is not the best fitted for making the ætherial solution:—

Finely powdered nitrate of potash ..	40	parts by	weight.
Concentrated sulphuric acid*	60	...	...
Carded cotton	2	...	...

Mix the nitre with the sulphuric acid in a porcelain vessel, then add the cotton, and agitate the mass for three minutes by the aid of two glass rods. Wash the cotton, without first pressing it, in a large quantity of water, and when all acidity is removed (indicated by litmus-paper), press it firmly in a cloth. Pull it out into a loose mass, and dry it in a stove at a moderate heat.

The compound thus obtained is not pure fulminating cotton; it always retains a small quantity of sulphuric acid, is less inflammable than gun-cotton, and it leaves a carbonaceous residue after explosion. It has however in a remarkable degree the property of solubility in æther, especially when mixed with a little alcohol; and it forms therewith a very adhesive solution, to which the name of *Collodion* has been applied:—

Preparation of Collodion.

Prepared cotton	8	parts by	weight.
Rectified sulphuric æther	125	...	...
Rectified alcohol	8	...	...

Put the cotton with the æther into a well-stopped bottle, and shake the mixture for some minutes. Then add the alcohol by degrees, and continue to shake until the whole of the liquid acquires a syrupy consistency. It may then be passed through a cloth, the residue strongly pressed, and the liquid kept in a well-secured bottle.

Collodion thus prepared possesses remarkably adhesive properties.

* The common commercial acid will answer. When very weak, a longer immersion of the cotton is required.

A piece of linen or cotton cloth covered with it, and made to adhere by evaporation to the palm of the hand, will support, after a few minutes, without giving way, a weight of from 20 to 30 lbs. Its adhesive power is so great that the cloth will commonly be torn before it gives way. The collodion cannot be regarded as a perfect solution of the cotton. It contains, suspended and floating in it, a quantity of the vegetable fibre which has escaped the solvent action of the æther. The liquid portion may be separated from these fibres by a filter, but it is doubtful whether this is an advantage. In the evaporation of the liquid, these undissolved fibres, by felting with each other, appear to give a greater degree of tenacity and resistance to the dried mass.

In the preparation of collodion it is indispensable to avoid the presence of *water*, as this renders it less adhesive; hence the æther as well as the alcohol should be pure and rectified. The parts to which the collodion is applied should be first thoroughly *dried*, and no water allowed to come in contact with them until all the æther is evaporated.—*London Medical Gazette.*

On the Preparation of the Black Sulphuret of Mercury. *By* C. Vogler.

The ordinary process for the preparation of mineral ethiops consists in triturating, in a porcelain or marble mortar, chemically pure metallic mercury with washed flowers of sulphur. The mixture is sprinkled from time to time with water or spirits of wine, and the trituration is continued until not a globule of mercury can be perceived with the aid of a lens. This process however cannot be recommended, for when the mixture is not sufficiently moistened a portion is carried away as dust, occasioning not merely a loss of material, but also exposing the operator to the serious inconvenience of inhaling mercurial vapour. To obviate this, the author recommends the following plan:—4 oz. of purified mercury and 1 oz. of flowers of sulphur, washed and passed through a very fine sieve, are introduced into a tolerably thick glass vessel capable of holding from 12 to 16 oz.; the mixture is then agitated constantly for about two hours, after which another ounce of sulphur is added at intervals; it is again shaken until no mercury can be discovered with the naked eye, after which the two remaining ounces of sulphur are added, and the mixture again shaken until no mercury can be perceived with the lens. This method requires less time than that by trituration, is more easy, and less injurious to the health.—*Journ. de Pharm.*, Sept. 1848.

Preparation of Ferridcyanide of Potassium on a small Scale. *By* T. B. Kolb.

Instead of passing chlorine into the solution of ferridcyanide of potassium, the author recommends boiling it with chlorate of potash and muriatic acid.—*Jahrb. für Prakt. Pharm.*, xvi. p. 338.

THE CHEMICAL GAZETTE.

No. CXLV.—November 1, 1848.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of the Pentachloride of Phosphorus upon Organic Substances. *By* A. CAHOURS.

IN this treatise the author shows that several organic substances belonging or closely related to the benzoyle series, for instance the aldehydes with 2 or 4 atoms of oxygen, which are generally comprised under the formulæ $C^m H^n O^2$; $C^{m'} H^{n'} O^4$, and their acids $C^m H^n O^4$ and $C^{m'} H^{n'} O^6$, when mixed with the pentachloride of phosphorus, constantly part with 2 atoms of oxygen, and take up 2 atoms of chlorine, either in their place or according to ordinary substitution, the pentachloride of phosphorus, PCl^5, being converted into oxychloride of phosphorus, $PCl^3 O^2$. Thus, I. oil of bitter almonds, II. benzoic acid, and III. anisic acid, furnish with pentachloride of phosphorus the following substances:—

I. $C^{14} H^6 O^2 + PCl^5 = PCl^3 O^2 + C^{14} H^6 Cl^2$ (chlorobenzole).
II. $C^{14} H^6 O^4 + PCl^5 = PCl^3 O^2 + C^{14} H^5 ClO^2$ (chloride of benzoyle) $+ HCl$.
III. $C^{16} H^8 O^6 + PCl^5 = PCl^3 O^2 + C^{16} H^7 ClO^4$ (chloride of anisyle) $+ HCl$.

Cahours prepared in the same manner the chloride of cinnamyle and the chloride of benzile. These and analogous compounds then afforded, when treated with cyanide of potassium and sulphuret of potassium, the corresponding cyanogen and sulphur compounds. With aniline they furnish new bodies corresponding to benzanilide. The pentachloride of phosphorus, on the other hand, appears not to act on a certain class of bodies which undoubtedly contain the oxygen in a different form; probably they do not contain the oxygen in the form of water.

Action of the Perchloride of Phosphorus upon the Oil of Bitter Almonds.—When chloride of phosphorus, PCl^5, is mixed in a retort with oil of bitter almonds, so much heat is evolved that it begins to distil over. If the reaction is assisted by a gentle heat, a mixture of two substances passes over, one of which boils at 226°–234° F., the other between 403° and 406°. The first constitutes about a fourth of the whole, and is the *oxychloride of phosphorus*, $PCl^3 O^2$, discovered by Wurtz. The second, with the higher boiling-point, is obtained, after distilling off the first, by mixing the residue with water.

The mixture evolves considerable heat and is greatly diminished in volume; an oily residue is obtained, which, after washing with alkaline, then with pure water, and drying over chloride of calcium, boils constantly at the above-mentioned temperature. The distillate is a new substance, an oil of bitter almonds with its oxygen replaced by chlorine, and is called chlorobenzole.

Chlorobenzole, $C^{14} H^6 Cl^2$, is a clear colourless liquid, which in the cold has a faint odour, but when warm it becomes highly penetrating, and the vapour is excessively irritating. The specific gravity is 1·245 at 61°, that of the vapour 5·649; and according to a second determination with vapour at a temperature of 527°, 5·625. Chlorobenzole is insoluble in water, but easily soluble in alcohol and æther. Caustic potash has no action upon it even with the assistance of heat. The analysis afforded the following results:—

Carbon	52·36	52·21	..	..	14	=1050·0	52·26
Hydrogen....	3·76	3·81	..	..	6	75·0	3·72
Chlorine	..	..	43·80	43·92	2	885·0	44·02

The calculated density of the vapour is 5·595, on the supposition that the formula represents 4 vols. of vapour.

The action of the chloride of phosphorus, PCl^5, upon the oil of bitter almonds may be expressed, according to what has been above stated, by the following equation:—

$$PCl^5 + C^{14} H^6 O^2 = PCl^3 O^2 + C^{14} H^6 Cl^2.$$

Sulphobenzole, $C^{14} H^6 S^2$, is a second new substance which the author obtained from chlorobenzole by treating it with the double sulphuret of potassium and hydrogen. The reaction gives rise to chloride of potassium and sulphobenzole, which forms a white nacreous substance, insoluble in water, and which is consequently easily obtained pure. Sulphobenzole is sparingly soluble in cold, but very readily in hot alcohol, and separates from the latter solution on cooling in shining scales. It melts at 147°, and solidifies on cooling to a crystalline mass. At a higher temperature it begins to volatilize, but turns brown and is partially decomposed. Even dilute nitric acid acts violently upon it, giving rise to the production of sulphuric acid and a yellow substance crystallizing in brilliant scales, which dissolves in alkalies. The following are the analytical results which led to the formula above advanced:—

Carbon	68·58	68·65	..	14	=1050·0	68·89
Hydrogen	4·99	4·92	..	6	75·0	4·92
Sulphur	..	..	26·00	2	400·0	26·19

Sulphobenzole is therefore an oil of bitter almonds, in which the oxygen is replaced by sulphur.

Action of the Chloride of Phosphorus, PCl^5, upon Benzoic Acid.—When benzoic acid is mixed in the form of powder with pulverized pentachloride of phosphorus, the two bodies do not act upon each other in the cold; but if the temperature is raised, a very lively reaction ensues, muriatic acid is given off; and when the operation is carried on in a retort, the receiver contains an acid clear

liquid, consisting of oxychloride of phosphorus, $PCl^3 O^2$, excess of pentachloride of phosphorus and chloride of benzoyle. The mixture is distilled again between 228° and 234°, to remove the oxychloride of phosphorus, after which nearly pure chloride of benzoyle passes over between 383°–392°; it is freed from minute traces of the other two bodies by washing with a little water, and is dried over chloride of calcium. It then boils at 385°, has a specific gravity of 1·25 at 59°, and its vapour that of 4·987 (temperature of the vapour 489°). The calculated density of its vapour is 4·901, assuming the formula to comprise 4 vols. vapour. The analysis, and indeed all its properties, agree with those of the chloride of benzoyle of Liebig and Wöhler, $C^{14} H^5 ClO^2$; it became changed by exposure to the air into muriatic and benzoic acids. When the liquid which is obtained in the distillation of benzoic acid with the pentachloride of phosphorus is mixed with absolute alcohol, the mixture becomes very much heated; if water is now added, the benzoate of the oxide of ethyle separates as a heavy oil of aromatic odour, which, after washing, drying and rectification, has the composition $C^{18} H^{10} O^4$; and boiled at 408°; its density was 1·05 at 59°. The same liquid afforded with dry ammonia benzamide, with aniline benzaniline; it is therefore undoubtedly the chloride of benzoyle. The reaction of the pentachloride of phosphorus upon benzoic acid may consequently be expressed in the following manner:—

$$PCl^5 + C^{14} H^6 O^4 = ClH + PCl^3 O^2 + C^{14} H^5 ClO^2.$$

The pentachloride of phosphorus acts in the same manner upon the benzoate of potash as upon benzoic acid; it does not affect either the benzoate of the oxide of ethyle or the methyle compound. With nitrobenzoic acid, on the contrary, it yields the following product—

Chloride of nitrobenzoyle, $Cl^{14} H^4 ClNO^6$, that is to say, a chloride of benzoyle in which 1 equiv. hydrogen is replaced by hyponitric acid, $C^{14} H^4 ClNO^4 O^2$. The pentachloride of phosphorus does not act in the cold upon nitrobenzoic acid, but at a gentle heat a liquid passes over, and the boiling-point rises gradually from 226° to 518°; the last portions are collected, washed with water, and dried over chloride of calcium. On rectification a yellowish liquid is obtained, which boils between 509°–514°. It is heavier than water, in which it is insoluble, and is gradually changed in moist air into muriatic and crystallized nitrobenzoic acid. It is very rapidly decomposed by a solution of caustic potash, yielding chloride of potassium and nitrobenzoate of potash. Analysis afforded—

Carbon	44·91	44·78	45·48	14	= 1050·0	45·25
Hydrogen	2·46	2·28	2·29	4	50·0	2·15
Chlorine.....	18·40	..	..	1	442·6	19·08
Nitrogen	7·39	..	..	1	177·0	7·63
Oxygen	..	..	..	6	600·0	25·89

Dry ammonia converts the chloride of nitrobenzoyle, $C^{14} H^4 NO^4 ClO^2$, into a solid mass, which is tolerably soluble in hot water, from which solution it crystallizes on cooling. It is probably the

nitrobenzamide recently described by Field, which he obtained by heating the nitrobenzoate of ammonia.

Action of the Chloride of Phosphorus upon Oil of Cinnamon and Cinnamic Acid.—Oil of cinnamon is violently acted upon by the pentachloride of phosphorus; a large quantity of muriatic acid is given off, and the mass becomes thick. When this mass is submitted to distillation, but a small quantity of liquid passes over, while the residue puffs up and becomes carbonized; for this reason no further experiments were made with this substance.

Cinnamic acid furnishes, in this respect, a purer result than its aldehyde, the oil of cinnamon; it behaves towards the pentachloride of phosphorus like benzoic acid; nearly the whole amount of the substance passes over, with an abundant evolution of muriatic gas, into the receiver, in which a mixture of oxychloride of phosphorus and chloride of cinnamyle collects.

Chloride of Cinnamyle, $C^{18} H^7 ClO^2$, is a hydruret of cinnamyle, in which 1 equiv. hydrogen is replaced by chlorine, and stands in the same relation to the hydruret as the chloride of benzoyle to the hydruret of benzoyle. It is obtained pure by collecting separately that which distils over between 481° and 509°, treating it with a small quantity of water, drying over chloride of calcium, and rectification. It then forms a light yellow liquid, which boils between 500° and 504°; its density at 61° is 1·207. It is very quickly decomposed in a moist atmosphere into muriatic acid and beautiful crystals of cinnamic acid. On analysis it afforded—

Carbon....	64·60	64·51	64·67	..	..	18	= 1350·0	64·90
Hydrogen..	4·05	3·93	4·03	..	..	7	87·5	4·20
Chlorine ..	..	..	..	21·60	21·20	1	442·6	21·28
Oxygen....	..	..	..	..	..	2	200·0	9·62

When alcohol is poured upon the chloride of cinnamyle, cinnamic æther is obtained, $C^4 H^5 O, C^{18} H^7 O^3$. When the chloride of cinnamyle is treated with dry ammonia, chloride of ammonium is formed, together with a substance analogous to benzamide, and which crystallizes from hot water. Chloride of cinnamyle evolves considerable heat with aniline, and forms with it

Cinnanilide, $C^{30} H^{13} NO^2$, which, after washing the product with water, then with alkaline water, and solution in alcohol, is obtained in slender acicular crystals. It melts at a somewhat high temperature, and distils without decomposition. It is scarcely affected by a solution of caustic potash; it is decomposed when heated with hydrate of potash into cinnamate of potash and aniline. It afforded on analysis—

Carbon	80·39	80·52	30	= 2250·0	80·66
Hydrogen	6·06	6·20	13	162·5	5·83
Nitrogen.....	..	6·41	1	177·0	6·35
Oxygen	..	..	2	200·0	7·16

Cyanide of Cinnamyle, $C^{20} H^7 NO^2$, is formed when the protochloride of cinnamyle is rectified over cyanide of potassium or cyanide of mercury; a liquid is thus obtained, which readily turns

brown in the air, and is decomposed into prussic and cinnamic acids. As above prepared it still contained some chlorine, on which account the results of the analyses did not agree well with theory.

Action of the Pentachloride of Phosphorus upon Oil of Cumin and Cuminic Acid.—When oil of cumin is mixed with pentachloride of phosphorus, considerable heat is disengaged, and on distillation nearly the whole passes into the receiver, in which two substances collect; the one boils at 232°; it is the oxychloride of phosphorus; the other between 500° and 509°. This substance is—

Chlorocuminole, $C^{20}H^{12}Cl^2$.—It is obtained pure when the immediate product of the distillation is washed with water, then with alkaline water, dried over chloride of calcium and rectified. It forms a liquid colourless substance, which possesses the peculiar odour of the chlorinated compounds of this class. It boils between 490° and 500°, is heavier than water, in which it is insoluble, but easily soluble in æther and alcohol. Solution of caustic potash appears not to act upon it. An alcoholic solution of the double sulphuret of potassium and hydrogen forms with it chloride of potassium and a tenacious mass of a disagreeable odour. As shown by the above formula, chlorocuminole differs from cuminole solely by the 2 atoms of oxygen being replaced by chlorine. The reaction may easily be expressed by the following equation:—

$$C^{20}H^{12}O^2 + PCl^5 = PCl^3O^2 + C^{20}H^{12}Cl^2.$$

Cuminole, the homologue of oil of bitter almonds, behaves therefore like the latter towards the pentachloride of phosphorus.

Cuminic Acid is acted upon by the pentachloride of phosphorus at a temperature of 122°–140°; a large amount of muriatic acid is disengaged; and on distilling the mixture, oxychloride of phosphorus, PCl^3O^2, and a second substance, the

Perchloride of Cumyle, $C^{20}H^{11}ClO^2$, pass over. This is obtained pure by washing with water those portions which distil over between 480° and 500°, drying it over chloride of calcium, and rectification. It is a colourless, very mobile liquid, with a specific gravity of 1·070 at 59°, boils at 493°–496°, and is converted in a moist atmosphere into muriatic and cuminic acids. This metamorphosis is effected more rapidly by ebullition with solution of caustic potash. It evolves considerable heat with alcohol, and on washing the product with water the æther of cuminic acid is obtained. The chloride of cumyle afforded on analysis—

Carbon	65·77	65·85	65·63	20	= 1500·0	65·79
Hydrogen	6·35	6·18	5·98	11	137·5	6·03
Chlorine	19·70	..	19·72	1	442·6	19·41
Oxygen	..	..	..	2	200·0	8·77

When the chloride of cumyle is treated with dry ammonia, the cuminamide recently prepared by Dumas from cuminic æther by means of ammonia, and by Field by heating the cuminate of ammonia, is obtained.

Cumanilide, $C^{32}H^{17}NO^2$.—The chloride of cumyle disengages considerable heat with aniline, and a substance analogous to benza-

niline is obtained, which, after washing with water containing a little alkali and repeated recrystallization from alcohol, separates in long silky needles resembling benzoic acid. This substance afforded on analysis—

Carbon	80·32	80·34	32 =	2400·0	80·15
Hydrogen	7·14	7·01	17	212·5	7·11
Nitrogen.....	6·08	..	1	177·0	5·92
Oxygen	..	..	2	200·0	6·69

Action of the Pentachloride of Phosphorus upon Benzilic Acid.—The pentachloride of phosphorus has a violent action upon benzilic acid; muriatic acid is copiously evolved, while oxychloride of phosphorus, $PCl^3 O^2$, and a second liquid with a higher boiling-point, pass into the receiver. This is the

Perchloride of Benzile, $C^{28} H^{11} ClO^4$.—That portion which passes over above 481° is collected separately, washed with cold water, and dried over chloride of calcium. After rectification it forms a colourless liquid with a powerful odour, which is heavier than water, and boils at 518°; it is converted in a moist atmosphere into muriatic and benzilic acids. A concentrated solution of caustic potash quickly forms with it chloride of potassium and benzilate of potash. Ammonia and aniline yield with it crystalline compounds, which were not further examined. Analysis afforded—

Carbon	68·36	68·41	28 =	2100·0	68·18
Hydrogen	4·38	4·58	11	137·5	4·46
Chlorine.....	14·00	..	1	442·6	14·35
Oxygen	..	..	4	400·0	13·01

Benzoine is likewise acted upon by the pentachloride of phosphorus. Oxychloride of phosphorus and several other products which were difficult to separate, and were not further examined, were formed.

Action of the Pentachloride of Phosphorus upon Anisic Acid.—The reaction between these two substances is violent; muriatic acid is disengaged, with formation of oxychloride of phosphorus and

Perchloride of Anisyle, $C^{16} H^7 ClO^4$.—This substance is obtained in a pure state when the portion which distils over between 480° and 518° is collected separately, and treated in the same manner as the substances previously described. It is a colourless liquid, with a very powerful odour and a specific gravity of 1·261 at 59°. It is soon decomposed in the air into muriatic and anisic acids. It forms with alcohol anisic æther, with disengagement of great heat; it behaves similarly towards pyroxylic spirit. It stands in the same relation to anisic acid as the perchloride of benzoyle to benzoic acid. On analysis it afforded—

Carbon	56·13	56·09	55·94	16 =	1200·0	56·33
Hydrogen	4·26	4·28	4·35	7	87·5	4·10
Chlorine.....	20·95	21·01	..	1	442·6	20·78
Oxygen.....	..	..	..	4	400·0	18·79

Anisamide, $C^{16}H^{9}NO^{4}$, is formed on treating the chloride of anisyle with dry ammonia. The mixture evolves considerable heat, and a solid substance soluble in alcohol is obtained, which crystallizes from the alcoholic solution in beautiful prisms. This compound may also be procured by treating anisic æther with ammonia. Analysis gave—

Carbon.....	63·43	16 =	1200·0	63·51
Hydrogen	6·01	9	112·0	5·95
Nitrogen	9·48	1	177·0	9·36
Oxygen	..	4	400·0	21·10

Anisanilide, $C^{28}H^{13}NO^{4}$.—Considerable heat is disengaged on mixing aniline with the chloride of anisyle, and a substance is obtained, which, after repeated crystallization from alcohol, forms acicular crystals, which sublime at a gentle heat, and are again deposited in very brilliant white needles. This substance afforded on analysis—

Carbon	74·16	73·71	28 =	2100·0	73·96
Hydrogen	5·83	5·87	13	162·5	5·72
Nitrogen.....	6·44	..	1	177·0	6·23
Oxygen	..	..	4	400·0	14·06

The Hydruret of Anisyle also yields oxychloride of phosphorus and a new product when mixed with the pentachloride of phosphorus, but the greater portion in the retort soon becomes black, and too little was obtained to submit the product to closer examination.

It is probable that a perchloride of nitranisyle corresponding to the perchloride of nitrobenzoyle exists, for on treating nitranisic acid with pentachloride of phosphorus, oxychloride of phosphorus and a dark yellow liquid are obtained. The latter boils at a much higher temperature, and is decomposed by exposure to the air into muriatic and nitranisic acids; it moreover yielded nitranisic æther with alcohol.

As regards the action of pentachloride of phosphorus upon such oxygenous bodies, it has been stated above that benzoic æther is not acted upon by it, which however is the case with benzoic and nitrobenzoic acids. Now if we write—

Benzoic acid	$C^{14}H^{5}O^{3}$, HO
Nitrobenzoic acid	$C^{14}H^{4}NO^{4}$, HO
Benzoic æther.....	$C^{14}H^{5}O^{3} + C^{4}H^{5}O$,

it is very easily explained why the pentachloride of phosphorus acts upon the two first bodies and not upon the last; as is well known, the pentachloride of phosphorus is readily decomposed by water, whilst the oxide of ethyle, which occupies the place of water in the last compound, has no action upon it. It is therefore probable that only those substances which contain oxygen in the form of water are decomposed by the pentachloride of phosphorus.

M. Cahours observes, in conclusion, that since the oxide of ethyle is not, while alcohol is, acted upon by the pentachloride of phos-

phorus, oxychloride of phosphorus, $PCl^3 O^2$, and muriatic æther resulting from the latter reaction—

$$C^4 H^6 O^2 + PCl^5 = PCl^3 O^2 + C^4 H^5 Cl + HCl,$$

the atom of oxygen in the æther cannot be contained in the same form as the second atom of oxygen in the alcohol. The experiments of Regnault and Malaguti upon the action of chlorine upon these two bodies are likewise in favour of this view, for they obtained with æther very simple products of substitution, whilst those originating from alcohol are far more complicated. This, in Cahours' opinion, is owing to the intervention of the atom of water, which gives rise to products of oxidation.—*Ann. de Chim. et de Phys.*, xxiii. p. 327.

Analysis of a Bituminous Coal from Barbadoes.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

My dear Sir,—The subject of the present notice, which was said to have been brought from the neighbourhood of Bridgetown, Barbadoes, was sent to our laboratory for analysis, as far back as the summer of 1845, by Thomas Daniel, Esq., of this city, a gentleman possessed of large estates in the West Indies. The publication of my results was however, from various causes, postponed for such a length of time, that it was not until my attention was arrested a few days ago by a paper on the "Ultimate Analysis of some Varieties of Coal," by Mr. Vaux, in the last number of the Quarterly Journal of the Chemical Society, that I was again reminded of the circumstance that they had not yet appeared in any of our scientific periodicals. I have therefore hastened to forward them to you for insertion in your excellent Journal.

The specimen examined was of a deep brownish-black colour, with a strong resinous lustre, and a faint and not unpleasant bituminous smell. It was exceedingly brittle, being easily crumbled to pieces between the fingers; the fracture was brilliant, but small and imperfectly conchoidal. When applied to the flame of a candle, it immediately ignited, burning with a bright smoky flame, and running down in drops like so much sealing-wax. The residuary coke possessed a semi-metallic lustre, was exceedingly hard, but porous, and was incinerated with much difficulty, leaving a small quantity of a reddish-gray ash, which did not fuse before the blowpipe.

Its degree of hardness was inferior to that of rock-salt.

Its mean specific gravity, as deduced from five experiments, was 1·115.

I. 200 grs. of the finely-powdered coal, when heated to about 220° F., lost 1·296 grs. of interstitial, or rather hygrometric moisture.

II. 300 grs., when treated as before, lost 1·944 gr. in weight.

III. 200 grs., when dried and heated to redness in a closed platinum tube, gave 78·82 grs. of coke.

IV. 300 grs., when treated as before, gave 117·897 grs. of coke.

V. 500 grs., when incinerated by passing a current of oxygen gas over it, whilst kept at a red heat, left 10·25 grs. of ashes.

VI. 259 grs., treated as before, left 5·060 grs. of ashes.

These experiments give the following composition per cent.:—

	I.	II.	III.	IV.	V.	VI.	Mean.
Moisture	0·650	0·646	..	..	..	..	0·648
Gaseous matter	..	..	..	..	..	..	59·998
Coke { Carbon..	..	..	39·410	39·299	..	..	37·352
Coke { Ash	..	..			2·050	1·954	2·002
							100·000

The ash was principally composed of silica, sulphate of lime and oxide of iron, with traces of sulphate of potash, chloride of sodium and phosphate of lime; there was no earthy carbonate present.

Upon an ultimate analysis of the dry coal, the following numbers were obtained:—

I. 3·04 grs., burnt with chromate of lead, gave 8·316 grs. of carbonic acid and 2·340 grs. of water.

II. 3·91 grs., burnt with oxide of copper and chlorate of potash, gave 10·752 grs. of carbonic acid and 3·026 grs. of water.

III. 4·01 grs., burnt with oxide of copper, &c., gave 11·011 grs. of carbonic acid and 3·100 grs. of water.

IV. 10·00 grs., burnt with potash and lime by Varrentrapp and Will's process, gave 1·110 grs. of ammonio-chloride of platinum.

V. 10·00 grs., burnt with potash and lime, gave 1·081 grs. of ammonio-chloride of platinum.

VI. 100 grs., deflagrated in the usual manner with a mixture of nitrate and carbonate of potash, &c., gave 0·135 gr. of sulphate of barytes.

VII. 120 grs. gave 0·169 gr. of sulphate of barytes, which give the following per-centage composition:—

	I.	II.	III.	IV.	V.	VI.	VII.	Mean.
Carbon ..	74·622	75·001	74·912	..	..	..	..	74·845
Hydrogen	8·555	8·601	8·592	..	..	..	..	8·582
Nitrogen	..	..	..	0·705	0·687	..	..	0·696
Oxygen ..	..	..	..	..	..	..	..	13·859
Sulphur ..	..	..	..	..	..	0·016	0·017	0·016
Ash	..	..	..	..	..	..	..	2·002
								100·000

I remain, my dear Sir,
Yours very truly,
THORNTON J. HERAPATH.

Mansion House, Old Park, Bristol,
October 11th, 1848.

On the Composition of the Butyrate of Copper. *By* M. LIES.

According to the observations of M. A. Laurent, the butyrate of copper is isomorphous with the acetate of the same base. Since acetic and butyric acids are homologous in the opinion of M. Ger-

hardt, I have determined the exact composition of the butyrate of copper, the water of this salt having never been ascertained. My analysis led exactly to the formula $C^8 H^7 O^3, CuO + Aq$, similar to that of the acetate $C^4 H^3 O^3, CuO + Aq$.

We have thus the first well-proved example of the isomorphism of two homologous salts containing the same amount of water of crystallization.—*Comptes Rendus*, September 25, 1848.

Discovery of Tellurium in Virginia. By C. T. Jackson.

Early in May last Mr. Knowles Taylor of New York gave me two specimens of native gold, in mica-slate rock, from an auriferous vein recently discovered in Whitehall, near Fredericksburg, Virginia. In one of the specimens I observed a considerable mass of a splendent foliated and sectile mineral, of the colour of antimony, which I recognised as an ore of tellurium. The gold was imbedded in a mass of it, and it was also observed to exist disseminated through the rock in shining metallic leaves. On submitting this mineral to analysis, I discovered that it was a *telluret of lead and gold*, or *foliated tellurium ore*. In the open glass tube before the blowpipe, telluric acid sublimes, and condenses in the cooler part of the tube in a yellowish-white film, which melts into drops. A little grayish sublimate also deposits, which is metallic tellurium. The residual matter, cupelled on mica, gave a well-characterized glass of litharge and a minute globule of pure gold. This interesting mineral has not, I believe, been heretofore discovered in the United States, and it is extremely rare in Europe. It had been mistaken for sulphuret of molybdenum, and was considered to be of no value. That error should be corrected, for it is not only valuable as an extremely rare mineral, but since, as I am informed, it occurs in abundance in the Virginia mine, it should be saved and wrought for gold, in the same manner as is practised in the tellurium and gold mines of Transylvania. It is very easy to expel the tellurium by heat, and then the gold may be obtained by the usual processes of amalgamation by mercury, and discharge of the mercury by heat. Since I detected the tellurium I have conversed with T. A. Dexter, Esq. of Boston, who has recently visited the mine, and has seen a considerable quantity of this tellurium ore in the vein. He gave me two very well-characterized specimens, which he took from the vein in place; so there can be no doubt of its existence in a true auriferous vein.—Silliman's *Journal*, September 1848.

On the Determination of the Proportion in which the Sulphur is contained in its two different Forms in the Sulphuretted Nitrogenous Organic Compounds. By T. H. Fleitmann.

It is well known that fibrine, albumen from blood and eggs, and caseine, when heated in a concentrated solution of caustic potash, are decomposed, and that a portion of the sulphur which these substances contain is eliminated, while another portion remains com-

bined with the organic substance. The eliminated sulphur converts a portion of the potash into sulphuret of potassium, exactly as if sulphuretted hydrogen had entered into combination with the potash. The condition of the sulphur which combines with the potash has been compared with that in which this element is contained in cystine. That sulphur which does not go to form sulphuret of potassium behaves in this respect like that in taurine. The determination of the relative proportion of the sulphur contained in these bodies in the two different states is not without interest in a physiological point of view.

I have attempted to solve the question in the following manner:— A weighed quantity of the comminuted substance was digested in a flask for some time with dilute caustic potash (solution of potash of 1·27 spec. grav., diluted with two volumes of water). When the mass had dissolved, it was mixed with a sufficient quantity of recently-precipitated hydrated oxide of bismuth, and digested with the same for six to eight hours at nearly a boiling temperature, or even carefully boiled upon the sand-bath with frequent agitation.

When, in this manner, the whole of the sulphur contained in the substance in that form had combined with the bismuth to form sulphuret of bismuth, the cold mass was supersaturated with acetic acid, and digested with it for some time, in order to render the mass capable of filtration and to dissolve the excess of oxide of bismuth. The organic substance, which is precipitated on saturation with acetic acid, dissolves readily in the excess. The washed sulphuret of bismuth with the filter was oxidized in a silver crucible by fusion with potash and nitre, and the sulphur, thus converted into sulphuric acid, determined in the usual way as sulphate of baryta.

I determined, according to this method, the amount of sulphur in the membrane of eggs, in fibrine, crystalline, albumen (from the blood of a donkey), and in caseine. The latter was prepared by precipitation with alcohol, washing with water, alcohol and æther. The membrane from eggs was prepared from egg-shells, which were rendered brittle by treatment with muriatic acid, and the shell removed by trituration and suspension. The following numbers were obtained:—

	Total amount of sulphur.	Sulphur from the BiO.		
Membrane, 4·14, 4·12, 4·10, 4·26 per cent.	2·61	2·47	2·45
Fibrine	0·52	0·53	0·50
Crystalline	0·34	0·37	
Albumen from blood	0·76	1·19	1·03
Caseine	0·07		

Ann. der Chem. und Pharm., lxvi. p. 380.

On two new Compounds derived from Morphine and Narcotine. *By* Messrs. Laurent *and* Gerhardt.

M. Arppe described, in 1845*, a peculiar substance obtained by treating morphine with an excess of sulphuric acid. He assigns to

* Chem. Gaz., vol. iii. p. 430.

the compound the formula $4(C^{35}\,H^{40}\,NO^6) + 5SO^3$, which is without its analogue among organic compounds. Considering the manner in which this substance is produced, we imagined it would present a composition similar to that of the amides and anilides; our experiments favour this supposition. We have also obtained a perfectly similar compound with narcotine.

Sulphomorphide.—We prepared this substance according to the process described by M. Arppe, by treating morphine with a slight excess of sulphuric acid. When recently prepared it is white, but it turns green in the course of time even in hermetically-sealed tubes. This colour is immediately produced by drying the product between 266° and 302°. It is persistent, and does not appear to be owing to the action of the atmosphere, for the corresponding product, prepared with narcotine, is immediately obtained of a deep green colour.

Sulphomorphide is not volatile; when heated upon platina foil, it leaves a bulky cinder extremely difficult to burn. Our analyses yielded,—carbon, 63·0; hydrogen, 5·8; sulphur, 5·4; results which lead to the following relations:—$C^{34}\,H^{36}\,N^2\,O^8\,S$, *i. e.* the formula of the neutral sulphate of morphine less 2 equivs. water:—

$$SO^4\,(H^2, 2C^{17}\,H^{19}\,NO^3) - 2OH^2.$$

Sulphonarcotide.—When narcotine, moistened with water, is heated with a slight excess of dilute sulphuric acid, a solution is obtained which becomes dark green by the further application of heat, and finally thickens. No gas is disengaged in this reaction. It is diluted with water and boiled, when nearly the whole dissolves. On cooling, the liquid deposits an amorphous powder of a dark green colour; it is thrown upon a filter, and washed with cold water, in which it is insoluble. It also dissolves in alcohol, but does not crystallize from it. In its behaviour it resembles sulphomorphide; when heated upon platina foil it leaves a bulky cinder difficult to burn. On distillation it disengages water, and some brown oily substances of a very disagreeable odour.

Analysis gave,—carbon, 59·1; hydrogen, 5·3; sulphur, 3·6; numbers which correspond to the formula $C^{46}\,H^{48}\,N^2\,SO^{16}$, represented by the neutral sulphate of narcotine less 2 equivs. water:—

$$SO^4\,(H^2, 2C^{23}\,H^{25}\,NO^7) + 2OH^2.$$

Ammonia is without action upon sulphonarcotide; caustic potash dissolves it with a brown colour, acids again precipitate it as a green powder. When boiled with nitric acid, it gives sulphuric acid and a yellow substance soluble in ammonia.

Sulphomorphide and sulphonarcotide evidently belong to the same class of substances as the amides and anilides; they are to the sulphates of morphine and narcotine what sulphamide and sulphanilide are to the neutral sulphates of ammonia and aniline. It was, it is true, found impossible to separate the morphine and narcotine; but it should be borne in mind, that, in the case of the anilides, this regeneration requires the intervention of a high temperature, and that this would necessarily destroy the fixed alkaloids, as morphine and narcotine.—*Journ. de Pharm.*, Oct. 1848, p. 302.

On the Identity of the Picric, Chrysolepic and Nitrophenissic Acids. *By* Prof. R. F. Marchand.

The author has confirmed by further experiments the identity of Dr. Schunck's chrysolepic acid with the picric or nitrophenissic acid. The form of the crystals of chrysolepic acid was found to be perfectly identical with that of picric acid measured by Prof. Mitscherlich.

The same conclusions have also been arrived at by M. E. Robiquet, by the analysis of the salts of lead. The point may therefore be now looked upon as settled.—*Journ. de Pharm.*, Oct. 1848, p. 318.

Analyses of the Waters of the River Exe and of the Bath Water-Works. *By* Thornton J. Herapath, Esq.*

I. *Water of the River Exe.*

The sample operated upon was taken from the middle of the river at Exeter, just above the bridge, during high-tide, on the 1st of August last.

An imperial gallon, or 70,000 grs., was found upon analysis to contain—

Carbonic acid gas at 55° F., 7·016 cubic inches.

Fixed constituents:—

Chloride of calcium	traces.
Chloride of magnesium	0·640
Sulphate of magnesia	0·160
Sulphate of soda	0·080
Crenate and apocrenate of magnesia	traces
Organic matter	1·600
Nitrate of lime	0·160
Carbonate of potash	traces
Chloride of sodium	4·240
Carbonate of lime	0·896
Carbonate of magnesia	0·064
Carbonate of protoxide of iron	traces
Sulphate of lime	3·040
Phosphate of lime	very minute traces
Silica	traces
	10·880

As the principal object of the inquiry was to ascertain, if possible, whether the water contained such a large proportion of organic matter as, from its tendency to putrefy, would render it unfit for the purposes of the brewer, a portion of the water was taken, and tested with chloride of gold in the manner described by M. A. Dupasquier†, when by the brownish-red tint assumed by the solution, after ex-

* Communicated by the Author.

† Comptes Rendus, April 5th, 1847; also Chem. Gaz., No. 109, p. 185.

posure to the light of the sun, an abnormal quantity of organic matter was proved to be present.

In order to determine the proportion of the nitrogenized matters contained in the water, the salts which remained after the evaporation of an imperial gallon of the water were taken, and burnt with potash and lime; they furnished 5·44 grs. of ammonio-chloride of platinum, corresponding to 0·336 gr. of nitrogen or 0·400 gr. of ammonia.

II. *Water from Beacon Hill, near Bath.*

The specimen of the water forwarded to us was said to be similar to that usually supplied by the corporation to the citizens of Bath.

It was collected on March 22nd, 1848.

There being a slight perforation of the cork of the bottle in which the water was sent to us for analysis, it was considered useless to attempt to ascertain the proportion of gaseous carbonic acid.

An imperial gallon of the water contained of—

Chloride of calcium Chloride of magnesium	1·120
Sulphate of soda with some sulphate of magnesia	0·320
Crenate of magnesia	0·080
Apocrenate of magnesia	0·040
Nitrate of lime or magnesia	traces
Nitrogenous organic matter	a little
Carbonate of potash	0·010
Chloride of sodium	4·000
Carbonate of lime	11·200
Carbonate of magnesia	very minute traces
Carbonate of the protoxide of iron	0·012
Sulphate of lime	4·480
Phosphate of lime	none
Bitumen?	traces
Silica	traces
	21·262

Mansion House, Old Park,
Bristol, October 16th, 1848.

On two new Substances belonging to the Amylic Series.
By O. Henry, Jun.

Bisulphuret of Amyle.—When equal volumes of crystallized sulphoamilate of potash and highly-concentrated bisulphuret of potassium are submitted to distillation, the products are water and a yellowish oily liquid, lighter than water, and which disengages a very strong and penetrating odour. It is the bisulphuret of amyle.

When distilled two or three times over fused chloride of calcium, the bisulphuret of amyle furnishes two products; the first boils between 412° F. and 464°, and is of a faint yellow colour; the second boils between 464° and 500°, and forms a beautiful yellow liquid. Both possess the odour above-mentioned.

The density of the bisulphuret of amyle boiling between 464° and 500°, was found to be 0·918 at 68°. On analysis with oxide of copper it furnished the following results:—

	Found.	H=1.		Calculated.
Carbon	58·90	10	= 60	58·3
Hydrogen	10·43	11	11	10·6
Sulphur	30·67	2	32	31·1

Sulphocyanuret of Amyle.—When nearly equal volumes of sulphoamilate of potash and sulphocyanide of potassium, both in the crystalline state, are well mixed and conveyed into a large retort provided with a cooled receiver, there is obtained, upon heating the mixture, water and a yellowish-white oily liquid, lighter than water and diffusing a penetrating alliaceous odour, although less strong than the preceding compound; it is the sulphocyanide of amyle. When frequently digested over fused chloride of calcium and distilled, it yields a colourless very mobile liquid, which begins to boil at 338°, and rises to 500°. I collected the portion boiling between 383° and 412°, and analysed it by combustion with oxide of copper. The following numbers are, like the above, the mean of several analyses:—

Carbon	56·86	12	= 72	55·8
Hydrogen	8·80	11	11	8·5
Nitrogen	..	14	14	10·9
Sulphur	..	32	32	24·8

The second portion which passed over was again digested with fused chloride of calcium, when it gave a colourless product, which boiled between 392° and 464°, and possessed a similar odour to that of the first product, although less disagreeable.

The density of the product which passed over between 412° and 464° was found to be 0·905 at 68°.

In the ethylic series, when bisulphuret of ethyle, mercaptan, or the sulphocyanuret of ethyle is boiled with nitric acid, *sulphoetholic acid* is obtained, which furnishes with bases beautifully-crystalline salts. Its homologue, the *sulphomethotic acid*, exists in the methylic series, and is prepared in a similar manner by treating with nitric acid the mercaptan, the bisulphuret, or the sulphocyanuret of this series.

It is remarkable, that neither the monosulphuret of ethyle nor the monosulphuret of methyle afford similar results with nitric acid, which has no action upon them. The same is the case with the monosulphuret of amyle; but amylic mercaptan furnishes the *sulphoamylotic acid* obtained by Gerathewohl, which is analogous with the two preceding acids, and likewise furnishes well-crystallized salts. I conceived that the two substances which I have obtained would likewise furnish the same acid; and on saturating with baryta I obtained the sulphoamylolate of baryta, which left, upon calcination in a platinum crucible, a residue of sulphate of baryta, in accordance with the number indicated by theory.—*Journ. de Pharm.*, Oct. 1848, p. 247.

✓ *On the Preparation of Cyanate of Potash and Urea.*

By C. Clemm.

In the preparation of the cyanate of potash by oxidation of the yellow prussiate, that portion of the cyanogen which is in combination with the iron is lost; there is likewise more or less loss incurred by the further oxidation of the cyanate of potash, which is converted into carbonate of potash and nitrogen. To turn to account the whole of the cyanogen of the prussiate, it will certainly be most advantageous to oxidize Liebig's cyanide of potassium, and to employ the amount of oxygen calculated for the cyanide of potassium in the form of some metallic oxide. If it were possible to reduce the cyanide of potassium, still mixed with the iron, easily to a powder, and then to mix it intimately with the requisite amount of metallic oxide, the object would be best attained by fusion; as this however is not easy of execution, it was sought to be attained by adding with proper care the requisite amount of metallic oxide to recently-fused cyanide of potassium. By the advice of Prof. Liebig I tried minium.

With the cyanide of potassium, obtained from 8 parts of anhydrous prussiate and 3 parts of carbonate of potash, theory requires for its oxidation 15 parts of minium, and it should yield $10\frac{1}{2}$ parts of cyanate of potash. To oxidize the cyanide of potassium, the crucible is removed from the fire, allowed to cool somewhat, and the 15 parts of minium gradually added, with constant stirring, to the still fluid mass. On the addition of each fresh portion of minium, the mass becomes more fluid, the minium is instantly reduced, and some gas is evolved, owing to a small quantity of the cyanate of potash in contact with the minium being oxidized to carbonate of potash, carbonic acid and nitrogen. If care be taken not to let the temperature of the mass become too high from the addition of too large portions of minium, the disengagement of gas is inconsiderable. When this operation is complete, the crucible is again placed in the fire, the mass well stirred, then poured out and allowed to cool in a covered vessel.

The cyanate of potash may be obtained from the cold pulverized mass by exhaustion with boiling spirit according to Wöhler's method. If the mass is to be used for the preparation of urea, it is exhausted with cold water until the extract no longer disengages cyanic acid upon the addition of an acid; it is then treated according to the method described by Prof. Liebig, that is to say, the requisite quantity of the sulphate of ammonia (8 parts for the above proportions) is dissolved in the last wash-water, which is then mixed with the other solution of the cyanate of potash, evaporated in the water-bath, and the crystals of the sulphate of potash separated by cooling from the solution of urea; this is evaporated in the water-bath nearly to dryness, and then repeatedly exhausted with boiling alcohol. If the alcoholic solution contain any prussiate, which may have been again formed on exhausting the cyanate of potash from any undecomposed cyanide of potassium and protoxide of iron, it is most easily removed by the careful addition of the sulphate of the

protoperoxide of iron. The prussian blue very soon subsides; the clear solution may be almost entirely decanted, and only the last portion filtered. After cooling, the alcoholic ley is separated from the crystals, the alcohol removed by distillation; the residue contains the remainder of the urea. In this manner from 4 to 5 parts of urea may be obtained from 8 parts of anhydrous prussiate of potash.

The sulphate of potash obtained in this operation is coloured red by a peculiar substance, which does not dissolve in boiling water, and may therefore be obtained in a pure state by filtration and washing. It appears to be a cyanogen compound of copper and iron, which was dissolved in the alkaline solution of the cyanate of potash, and separated on evaporation upon the expulsion of the ammonia. It dissolves partially in caustic potash; the solution turns blue by exposure to the air; on the addition of a little acid a bluish-white substance separates, which turns light red on the addition of more acid, and dark red with a large excess; the paler colour is restored on the addition of caustic potash. The filtrate of the first acid solution of this substance quickly turns blue in the air, and instantly yields with salts of iron a copious blue precipitate, a proof consequently that prussiate of potash must have been formed by the treatment with caustic potash. The red substance, when purified from sulphate of potash by washing, burns upon platinum foil, leaving a residue which consists principally of iron and a little copper. —*Ann. der Chem. und Pharm.*, lxvi. p. 382.

ANALYTICAL CHEMISTRY.

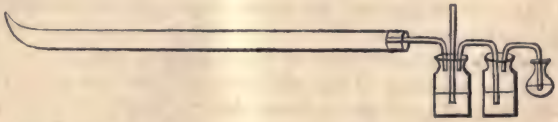
On the Estimation of Nitrogen. By C. Nöllner.

Having for many years been engaged in the manufacture of prussiate of potash, my attention has been especially directed to the ascertaining the amount of nitrogen in the substances used in this process, as the relative value of the raw materials relatively to the produce of prussiate of potash principally depends on this point.

Will and Varrentrapp's process is somewhat tedious and expensive; the following, which I can recommend from more than six years' experience, is easier, requires no evaporation, avoids any danger of the ascent of the acid liquid into the combustion-tube, loss of platina, and especially of time. Ignite the nitrogenous substance in an ordinary combustion-tube with hydrate of lime or with soda-lime (I prefer the hydrate of lime); but instead of passing the generated ammonia into muriatic acid, I employ a solution of pure tartaric acid in absolute alcohol; so that the ammonia disengaged is instantly converted into bitartrate of ammonia, and deposited in the form of a crystalline powder, which is perfectly insoluble in absolute alcohol

As the bitartrate of ammonia contains 10·2 and the ammonio-chloride of platinum contains only 7·6 per cent. ammonia, it may b objected to this method that it is less accurate; but if, on the other hand, it be considered that a loss is more easily avoided by simpli-

fying the method; that pure tartaric acid is more readily obtained than pure platinum or pure chloride of platinum; that, moreover, the bitartrate of ammonia has a far less specific gravity than the ammonio-chloride of platinum, so that with the same quantity of ammonia a far more bulky precipitate is obtained; I think this method, which has constantly afforded me satisfactory results, may be recommended not only to those engaged in manufacturing processes, but to chemists occupied in the most accurate investigations. As it would be difficult to remove the precipitate from the absorption apparatus in general use, I employ two wide-mouthed bottles, each of which contains from half an ounce to three-quarters of an ounce of absolute alcohol, in which so much tartaric acid is dissolved, that at the end of the operation an excess of tartaric acid is present.



The tube, curved at right angles, passing from the combustion-tube into the first bottle, must not dip into the tartaric acid solution, as it would soon become stopped by the separation of the salt, and the solution of the tartaric acid would ascend on the cooling of the combustion-tube. The pneumatic tube connecting the first bottle with the second need only dip a few lines into the liquid of the second glass, and to avoid any stoppage, should not be too narrow—about the diameter of an ordinary writing-pen. Into the cork of the first bottle a safety-tube is inserted, which is immersed in the liquid; and to be sure that no ammonia is lost, the second bottle is connected with a third, in which however, when the firing is well conducted, no precipitate is ever seen to form. Should the aperture of the pneumatic tube show signs of becoming stopped up, it is only requisite to blow gently into the safety-tube to remove instantly the film of tartrate of ammonia.

As shown by Varrentrapp and Will, towards the end of the operation, especially with substances containing much carbon, a quantity of free hydrogen gas is given off, owing to the decomposition of the hydrate water of the alkali. I have had frequent opportunity of observing this phænomenon. Now this evolution of hydrogen, and also of aqueous vapour from the excess of hydrated lime, so completely expels the whole of the ammonia, that it appeared to me quite superfluous to break off the pointed end of the combustion-tube, and to draw the air contained in it through the tartaric acid solution; at all events, in investigations for technical purposes, it suffices, by removing some of the incandescent coals, to allow cold air to pass in through the safety-tube, and then to drive it through the acid solution by the re-application of heat. When all evolution of gas has ceased, I allow the apparatus to remain connected until it has acquired so low a temperature that it may easily be taken to

pieces. The precipitate is then collected upon a weighed filter, an alcoholic solution of tartaric acid added to the liquid which passes through, to see whether any further precipitate is produced, and the precipitate then washed with *absolute* alcohol until what passes through no longer exhibits any acid reaction. As the precipitate is crystalline, it is very soon washed, and not less quickly dried in the water-bath at 212° F.

The nitrogen is then easily calculated from the known composition of the bitartrate of ammonia with 1 equiv. water. According to Dulk, 100 parts contain—

10·2 ammonia = 8·4 nitrogen,
79·0 tartaric acid, and
10·7 water.

The amount of nitrogen in the following substances, as they usually occur in commerce and are employed for manufacturing purposes, was ascertained in this manner. The results are of no value to the purely scientific man, but are of great interest, not merely to the manufacturing chemist, but also to agriculturists, many of the substances being frequently employed as manures.

2·7 grms. horn-shavings furnished 3·36–3·39 bitartrate of ammonia, corresponding to 10·46 per cent. nitrogen.

2·7 grms. woollen rags furnished 3·29 bitartrate of ammonia, corresponding to 10·0 per cent. nitrogen.

2·7 grms. bristles furnished 3·12 bitartrate = 9·7 per cent. nitrogen.

2·7 grms. whalebone gave 2·87 bitartrate = 8·93 per cent. nitrogen.

2·7 grms. old shoes and other old leather gave 2·15 bitartrate = 6·68 nitrogen.

2·7 grms. animal charcoal, which had served in the manufacture of prussiate of potash, afforded 0·32 bitartrate of ammonia, corresponding to 0·98 per cent. nitrogen.

2·7 grms. bone-charcoal gave 0·40 bitartrate of ammonia = 1·1 per cent. nitrogen.—Liebig's *Annalen*, lxvi. p. 314.

On the Estimation of Molybdic Acid. *By* Prof. H. Rose.

As molybdic acid is volatilized at a high temperature, especially with access of air, in considerable quantity, its estimation is rather a difficult matter. Molybdic acid may, it is true, be precipitated from dilute acid solutions by a current of sulphuretted hydrogen in the state of brown sulphuret. However, this precipitation is accompanied with great inconvenience, as it is excessively difficult to convert the molybdic acid wholly into the state of sulphuret.

The author found the best method of determining molybdic acid quantitatively was to convert it into molybdic oxide, which is most readily effected by heating it in an atmosphere of hydrogen. On heating it over a spirit-lamp at not too high a temperature, there need be no fear of small quantities of metallic molybdenum being formed with the oxide. The heating may be effected in a platinum crucible with a perforated lid, through which the hydrogen is con-

veyed into the crucible. Heat is applied until the weight of the oxide of molybdenum remains constant.

If a liquid contain molybdic acid dissolved in ammonia, it is carefully evaporated to dryness, and the dry mass heated in the same manner as pure molybdic acid in an atmosphere of hydrogen, to convert it into oxide. This operation may also be carried out in a platinum crucible.

When the molybdic acid is contained in an alkaline solution, it may be entirely precipitated by a solution of protonitrate of mercury after the liquid has been neutralized with nitric acid. If any alkaline carbonate were present, the solution, after saturation with nitric acid, is kept from twelve to twenty-four hours in a moderately warm place, in order to expel the whole of the carbonic acid. The precipitate of the protomolybdate of mercury is of a yellow colour and very bulky, but after standing for some hours sinks very much together. It is collected on a weighed filter, and washed with a very dilute solution of the protonitrate of mercury, as it is somewhat soluble in pure water. After being perfectly dried at 212° and accurately weighed, the precipitate is removed from the filter, and treated in a platinum or porcelain crucible with hydrogen in the same manner as molybdic acid or the molybdate of ammonia; oxide of molybdenum is obtained; that which remains adherent to the filter is weighed with it, and the quantity of molybdic oxide contained in it calculated.

By this method it is possible to determine accurately at the same time the amount of fixed alkali which was combined with it. Sulphuric acid is added to the liquid filtered from the protomolybdate of mercury, and the whole concentrated by evaporation. Protosulphate of mercury separates, which is converted, on the evaporation of the liquid, into yellow basic sulphate of mercury. The dry mass is exhausted with hot water, the yellow residue separated by filtration, and the filtered liquid evaporated to dryness. The dry mass may be converted in the usual manner, by treatment with carbonate of ammonia, into neutral alkaline sulphate.

The combinations of molybdic acid with the fixed alkalies may also be decomposed by chloride of ammonium. They are mixed in the dry state with an excess of an ammoniacal salt, and calcined with it. When the acid exists in the state of an acid salt, the mass does not fuse, but the acid is converted into molybdic oxide. It is mixed with fresh quantities of chloride of ammonium, and again calcined until no further increase in weight results. The ignited mass is treated with water, which leaves the molybdic oxide undissolved. It is collected on a weighed filter, and dried at 212°. The liquid separated from the molybdic oxide contains the alkali in the state of chloride.

This method does not afford such accurate results as the determination of molybdic acid by means of the protonitrate of mercury, a small portion of the acid being reduced by the chloride of ammonium to the state of metal. It may however be employed for those molybdates which are very sparingly soluble in water.—*Proceedings of the Berlin Academy*, July 1848.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Examination of Madder-Root. *By* H. Debus.

The material employed for these investigations was the best kind of Zealand madder. The roots were exhausted three or four times with from 15 to 20 times the amount of boiling water, and the extracts filtered through flannel; the last liquids were but slightly coloured. When these are boiled for some time with an excess of hydrated oxide of lead, a portion of the oxide dissolves, while another combines with the colouring principles, forming insoluble reddish-brown compounds. The liquid has now a pure yellow colour, and is no longer precipitated by salts of the heavy metallic oxides.

The lead precipitate, after being carefully washed, is decomposed by heating it with dilute sulphuric acid, when the pigments in combination with the oxide of lead are separated; and, as they are all very sparingly soluble in water, they may easily be freed from acid by washing with water. When they are now repeatedly exhausted with boiling alcohol, the insoluble residue consists of sulphate of lead coloured by a dark brown substance. The substance taken up by the liquid may be divided into two groups, the one, A, being precipitated from the solution by calcined oxide of zinc, the other, B, not. I shall reserve my observations on the latter for a subsequent communication.

To obtain the former, the alcoholic solution is agitated with small portions of oxide of zinc until it is no longer coloured red. To remove the oxide of zinc, which subsides with great difficulty, it suffices to boil the liquid for some time, when it then readily separates. The zinc compound obtained was washed with spirit, and then warmed with dilute sulphuric acid, when the pigments A separate, and the oxide of zinc passes into solution. If they are treated, after previous washing, repeatedly with æther, they are dissolved with the exception of a brown insoluble resinous substance. The solution in æther was precipitated with oxide of zinc, when a fatty substance remained in solution, coloured by a slight trace of the bodies B, which still adhered to the alcoholic solution of the group A. The compound is again decomposed with sulphuric acid, and the washed pigments repeatedly exhausted with a strong boiling solution of

alum, until the liquids, after long standing in the cold, deposit nothing further. A brownish-red substance separates from the first and second decoctions, which in the subsequent extracts becomes yellow. This yellow substance is boiled with dilute muriatic acid, in order to remove the alumina; the insoluble pigment is dissolved in boiling alcohol, from which on slow evaporation it crystallizes. By repeated recrystallization the pigment is obtained in splendid yellowish-red needles, several lines in length. This substance, which possesses acid properties and forms salts, I shall call *lizarinic acid.*

The alum solutions, from which the lizarinic acid has separated, are coloured dark red by a pigment which may be precipitated by the addition of some sulphuric acid; it however requires from twelve to twenty-four hours for its complete separation. The precipitate is exhausted with boiling dilute muriatic acid to dissolve out the alumina still contained in it, washed with water, and dissolved in from 150 to 200 times its amount of alcohol with the assistance of heat. After two or three hours the pigment separates from this solution in red needles from 2 to 3 lines long. I propose to call this substance *oxylizarinic acid.* This acid crystallizes more readily than the lizarinic acid, and may easily be separated from the minute traces of the latter, which were still contained with the oxylizarinic acid in the alum solutions, by the first crystallization. To obtain it perfectly pure, it is frequently recrystallized.

Lizarinic acid, obtained in the manner above described, dissolves very sparingly in the boiling alum solution, from which on cooling it separates almost entirely, while the oxylizarinic acid dissolves very readily in it with a dark red colour, without on long standing depositing anything, if too little alum liquid has not been employed. I obtained from 20 lbs. of madder between 4 and 5 grms. of the two acids. That which remained undissolved on boiling the pigments precipitated from the æthereal solution by oxide of zinc, is very readily soluble in æther, of a dark red colour, and mixed with lizarinic acid. All my experiments to separate these substances from each other did not lead to any favourable result.

I have just mentioned that only a portion of the substances precipitated by oxide of zinc from the alcoholic solution is soluble in æther. It consists of the above-mentioned substances. The insoluble residue is a mixture of resinous bodies, which I have not been able to separate. When it is boiled with alcohol a great portion of what is dissolved separates on cooling in brown flakes. If a part of the solvent be removed by distillation, a further quantity separates. I have made analyses of the two substances thus obtained, without however having any further guarantee of the purity of the products than that the two analyses give similar results.

	First separation.	Second separation.		
Carbon	64·89	65·32	60 =	65·09
Hydrogen	5·91	6·07	33	5·95
Oxygen	29·20	28·61	20	28·96

When the aqueous extract of the madder-root has been deprived of the above substances by long boiling with hydrated oxide of lead,

a yellow liquid remains, which was evaporated to a syrupy consistence, and then mixed with spirit. This produced an abundant gray precipitate, which contains oxide of lead in chemical combination, and is insoluble in water. Besides much pigment, this precipitate contains an acid which precipitates acetate of lead, and its ammoniacal salt, also the salts of the alkaline earths; but in all these combinations it is accompanied by the pigment, which cannot be removed even by digestion with animal charcoal. The quantity was too small to admit of a more accurate examination of its properties. The alcoholic liquid from which the preceding lead salt separated, contains sugar and a yellow substance which I could not obtain pure, but which gives a very interesting reaction with muriatic acid. When its solution is heated to boiling with muriatic acid, the liquid acquires a green colour; a dark green flocculent mass separates, which is insoluble in water and alcohol, turns red when treated with potash, is again precipitated green by acids, and appears to furnish very interesting products of decomposition with nitric acid. It furnished on analysis—

Carbon	63·94	63·67	30	= 63·82
Hydrogen	5·02	4·94	14	4·96
Oxygen	31·04	31·39	11	31·22

As it is, however, impossible to obtain this substance crystallized, or to produce combinations with it, no certainty can be derived from the analyses with respect to the correctness of the formula. A qualitative examination of the aqueous extract of the root for inorganic constituents detected a large amount of gypsum, which crystallizes on concentrating the extract to a syrupy consistence, sulphate of potash, phosphate of lime, chloride of potassium, silicic acid and alumina.

*Lizarinic Acid**.—This acid crystallizes from alcohol on slow evaporation in large crimson needles, which dissolve easily in æther and alcohol; more readily in hot than in cold water, and very sparingly in a boiling solution of alum, from which it again separates on cooling. Concentrated sulphuric acid dissolves lizarinic acid with an intense blood-red colour; on dilution with water, the pigment again separates unaltered. Its salts are red or violet, and with the exception of the potash, soda and ammonia salts, insoluble in water and in alcohol. When heated, lizarinic acid melts, and sublimes in reddish-yellow needles. Dilute nitric acid and chlorine appear to have no action upon it; a mixture of chromate of potash and sulphuric acid dissolves it, and produces some change; but unfortu-

* This substance is identical in its composition and its properties with the *alizarine* recently described by Schunck. The lime and baryta salts analysed by Schunck agree very well with the formula—

$C^{28} H^8 O^7 + 2CaO$ and $C^{28} H^8 O^7 + 2BaO$.

	Calculated.	Found.	
CaO	18·6	18·3	18·6
BaO	38·5	38·0	38·8

nately I was unable to examine the product of metamorphosis from want of material. On combustion with chromate of lead it gave:—

Carbon.....	68·95	68·98	68·98	30 =	68·70
Hydrogen.....	3·79	3·80	3·78	10	3·81
Oxygen.....	27·26	27·22	27·20	9	27·50

Lizarinate of Lead.—When a solution of acetate of lead in alcohol is added to an alcoholic solution of lizarinic acid, rendered slightly acid by acetic acid, taking care that the lizarinic acid is in excess, a copious, beautiful violet precipitate is formed, which is insoluble in water, but soluble in an excess of acetic acid and potash. This salt is not altered by exposure to a temperature of 320°. If too much acetate of lead is used in its preparation, the precipitate is always mixed with some basic acetate of lead. For analysis the salt was dried at 248°; it furnished—

Carbon	38·18	38·51	30 =	38·55
Hydrogen	1·97	1·98	8	1·71
Oxygen	..	..	7	11·98
Oxide of lead....	47·62	..	2	47·76

Oxylizarinic Acid.—This acid is distinguished from lizarinic acid by its ready solubility in a solution of alum; it is sparingly soluble in cold water, but easily soluble in hot. Potash, ammonia, soda, æther and alcohol dissolve it readily. Its salts behave like the lizarinates, and are scarcely to be distinguished from them by their external properties. Fuming sulphuric acid dissolves oxylizarinic acid without alteration; no reaction takes place even when the mixture is heated so that anhydrous sulphuric acid is expelled, and on diluting the liquid with water, unaltered oxylizarinic acid is separated; but if the temperature be raised to about 390°, sulphurous acid is given off, and the liquid becomes black. The acid employed for analysis, as well as its lead compound, were dried at 248°:—

Carbon.....	66·23	66·38	66·59	15 =	66·67
Hydrogen.....	3·73	3·87	3·87	5	3·70
Oxygen.....	30·04	29·75	29·54	5	29·63

Oxylizarinate of Lead.—What has been stated respecting the preparation and properties of the lizarinate of lead equally holds good for the oxylizarinate. It furnished on analysis—

Carbon	37·90	38·02	15 =	37·88
Hydrogen	1·72	1·87	4	1·68
Oxygen	..	..	4	13·48
Oxide of lead....	46·62	..	1	46·96

If we compare the formula of lizarinic acid with that of the oxylizarinic acid, it is seen that 1 atom of lizarinic acid requires 1 atom of oxygen to furnish the elements of 2 atoms of oxylizarinic acid. I have made some experiments to produce such a metamorphosis, without however obtaining any favourable result. Unfortunately I had too little material at my disposal to decide this question completely. If we may be allowed to draw a conclusion from the

changes which the madder-root undergoes when exposed to the influence of the atmosphere, it certainly does appear as if the one pigment were converted into the other by the assimilation of oxygen.

Of late a process described by Robiquet has been used in madder-dyeing to obtain a larger amount of pigment than was furnished by the hitherto usual method. The madder is macerated with concentrated sulphuric acid to destroy the woody fibre and other parts which are said to hold back some pigment. To ascertain the truth of this statement, madder was repeatedly extracted with cold, then with hot water, and lastly with alcohol as long as any pigment was removed. The roots were rendered almost colourless by this treatment, and yielded, after being acted upon by sulphuric acid, washing and boiling with water, some pectine but no pigment. It is evident therefore that the advantageous action of the sulphuric acid is different from that above given, and the reason appears to me to be the following:—When madder is extracted with cold water, and the extract set aside for twenty-four hours, or heated for some hours, as customary in madder-dyeing, a copious brown precipitate separates, and the liquid becomes faintly acid; this precipitate, which contains the above-described pigments, is insoluble in water and in alcohol, but dissolves readily in these media if it has been previously heated to boiling with sulphuric, muriatic or acetic acid. It is evident that by treating the substance with acids, the useful pigments are again rendered soluble, and separated from the body which causes their elimination from the colour-bath.

Kuhlmann admits the existence of malic acid in the aqueous extract of madder, founded upon the fact that it gives a precipitate with barytic water, which contains an organic acid resembling malic acid. In those kinds of madder which I have had an opportunity of examining, this precipitate is coloured, and contains only sulphuric and phosphoric acids.

Schiel prepared the so-called madder-purple and madder-red according to Runge's method, and submitted them to analysis. The above-mentioned substances behave however like lizarinic and oxylizarinic acid towards a solution of alum, and are likewise partially reprecipitated from this solution by sulphuric acid. In fact, by treating a solution of Runge's madder-red and madder-purple with oxide of zinc, it is possible to separate lizarinic and oxylizarinic acids, whilst the substances B remain in solution. When the mother-ley from the oxylizarinic acid is evaporated, it deposits a colourless gelatinous substance, which is insoluble in water, but was still mixed with a little oxylizarinic acid. An analysis of this substance gave the following result:—

Carbon	60·78
Hydrogen	4·87

When the original solution of the oxylizarinic acid is concentrated too far, the crystals of this acid are very much contaminated by the substance just described; a fact which may contribute to explain the differences between my analyses and those of Schiel.—*Ann. der Chem. und Pharm.*, lxvi. p. 351.

On some of the Proximate Principles of Vegetables, their Nature, and on a new Method of preparing them. *By* M. Lebourdais.

In 1825 I commenced a numerous series of experiments, with a view to obtain the proximate principles I imagined must exist in the Columbo root, the bulbs of *Scilla*, the leaves of *Digitalis*, of *Ilex*, the flowers of *Arnica*, &c. These experiments, although without satisfactory results, were nevertheless continued until 1840, when I gave up the use of chemical reagents, and resolved to try some substance which, possessing both a chemical and mechanical action, would have a kind of elective affinity, so as to seize hold of certain substances and eliminate others. After numerous experiments, I tried animal charcoal with perfect success. My first experiments with this reagent were made on a spirituous extract of Digitalis. The solution, which was not very highly coloured, having been previously precipitated with acetate of lead and filtered, was agitated with animal charcoal and the flask containing the mixture set aside; to my great astonishment, the liquid, on depositing the charcoal, had become not merely colourless, but had entirely lost its bitter taste. I decanted the liquid and washed the charcoal with distilled water, dried it in the stove, and then treated it with boiling alcohol, which acquired a pale tint, and took up the whole of the bitter principle. The alcohol, on evaporation in the water-bath, left at the bottom of the vessel an amber-coloured liquid, which deposited a pulverulent substance, the quantity of which increased after some time and cooling. This new substance, separated and washed, dissolved in alcohol, and furnished by its spontaneous evaporation crystals of digitaline. The crystals dissolve, but in small quantity, in water, to which they communicate a very bitter taste; they are more readily soluble in weak than in strong alcohol, and more so in hot than in cold. Æther has but little action upon digitaline. Both the alcoholic and the aqueous solution are neutral, as they have no action upon blue litmus-paper and upon that which has been reddened by an acid.

Sulphuric acid dissolves digitaline, and this solution finally acquires suddenly a very beautiful purple colour. After a time this colour disappears, passing into a brown, and a precipitate forms in the liquid of a blackish substance, produced by the decomposition of the proximate principle. If the purple solution of Digitalis in sulphuric acid is diluted with water, it instantly loses its colour, and acquires a yellowish-green one, resembling that of chlorine. Concentrated nitric acid dissolves it without assuming any colour; the same is the case with hydrochloric acid. No precipitate is formed by pouring ammonia into solutions of digitaline. The same was found to be the case with acetate of lead, lime-water, potash and soda. Digitaline did not appear to me to contain any nitrogen.

This process having furnished me with a very satisfactory result, I applied it, with certain modifications, to isolate other proximate principles, and always with success.

Ilicine.—2 lbs. of powdered holly-leaves, treated with boiling water, furnished a greenish decoction, which was very bitter; the

liquid was decanted, filtered, and boiled with animal charcoal, being stirred constantly. On removing the flask from the fire, the charcoal subsided, and the liquid, which had lost its colour and much of its taste, was decanted. The animal charcoal was washed, boiled, and treated with boiling alcohol, to which it imparted the bitter taste of the holly; the liquid was filtered, and the alcohol removed by distillation, when a colourless inodorous liquid remained at the bottom of the vessel, of a very bitter taste and a syrupy consistence. This solution was neutral; it furnished, on spontaneous evaporation or in the stove, a solid amorphous substance, of the appearance of gelatine, to which I have given the name of Ilicine. It is soluble in water and in alcohol; and although not hygrometric, I have not been able to obtain it in the crystalline state.

Scillitine.—A concentrated, highly-coloured and viscous decoction of the bulbs of squills was precipitated by acetate of lead (the viscosity of the liquid preventing the precipitation of the animal charcoal), and filtered. The resulting liquid was agitated in the cold with animal charcoal, and the vessel containing the mixture set aside; gradually the animal charcoal subsided, and carried down with it the bitter and colouring principles; the liquid was decanted, and the charcoal washed, dried and treated with hot alcohol, which became excessively bitter. After filtration the alcohol was removed by distillation, when a milky liquid remained in the retort, in which floated numerous minute particles of a whitish substance, sparingly soluble in water, to which it nevertheless imparted an intense bitter taste; it dissolved readily in alcohol, and the solution left an amorphous residue on spontaneous evaporation. The milky liquid evaporated in the hot chamber gave the same result. This substance is neutral, does not absorb moisture from the atmosphere, and produces on the tongue a sensation analogous to that caused by a caustic substance. Scillitine, as thus obtained, is solid, is readily decomposed by heat, dissolves in concentrated sulphuric acid, and appears to communicate to the solution a purple colour, which instantly disappears, and turns black, owing to decomposition. It is also dissolved by nitric acid, but decomposed at the same time.

Arnicine.—A concentrated infusion of the flowers of *Arnica montana* was gradually filtered through a thick layer of animal charcoal, which had been previously washed. The filtered liquid was deprived of the bitter and colouring principles. The charcoal, after being washed and dried, was treated with alcohol, to which it imparted the bitter taste of the Arnica. The alcoholic solution was filtered, and submitted to distillation; it left a milky liquid, which furnished on evaporation a substance having the appearance and consistence of turpentine. It is but very sparingly soluble in water, but nevertheless imparts to it a bitter taste. It dissolves in every proportion in alcohol; the solution, on spontaneous evaporation, leaves a residue of a syrupy consistence. Arnicine is neutral. Acetate of lead must not be used in the preparation of this substance, as the precipitate carries down with it nearly the whole of the arnicine.

Columbine.—An aqueous infusion of the Columbo root, obtained

by displacement, was filtered through a thick stratum of animal charcoal; in its passage it was deprived of its bitter taste and colour. The charcoal, after being washed and dried, was treated with alcohol, to which it communicated the colour and taste of the Columbo. This solution deposited minute crystals of columbine on spontaneous evaporation. If, instead of treating the charcoal with alcohol, a stream of water is passed through it as long as the liquid which filters has a bitter taste, the columbine is removed, but not the colouring substance, which may now be obtained separately by digesting the charcoal with alcohol. The columbine may thus be obtained perfectly pure and crystalline.

Colocynthine.—A concentrated infusion of the parenchyma of the fruits of the Colocynth was first precipitated with acetate of lead, filtered, and treated in the same manner as for the preparation of columbine. The solution obtained on spontaneous evaporation deposited the colocynthine in mammillated tufts.

Strychnine.—An infusion of nux vomica, treated in the same manner as the Columbo, furnished strychnine, with all the physical and chemical characters of that obtained by the processes hitherto employed—a proof of the pre-existence of alkaloids in vegetables.

Of the substances upon which I experimented only the three last were found to possess the property of combining with animal charcoal, and then leaving it when treated with water, and on treating this solution with charcoal again uniting with it.

The juices of hyoscyamus, hemlock, &c., treated in the same manner as the flowers of Arnica, yielded the principles of these plants, some in an amorphous, others in the crystalline state. Wishing to confirm as much as possible the undoubted existence of certain proximate principles in vegetables in the alkaloid state, I prepared morphine, narcotine and quinine by the same method. The experiments to obtain the latter appear to me to be conclusive.

500 grms. of *Cinchona calisaya* were exhausted with water, acidulated with sulphuric acid, and the acid decoction filtered through washed animal charcoal. The liquid, after having traversed the layer of animal charcoal, was insipid and colourless. The charcoal was washed and dried, and treated with alcohol of 0·848 spec. grav.; the alcoholic solution furnished, on evaporation in the water-bath, a milky liquid, and the sides of the vessel were covered with crystals of quinine. The milky liquid turned red litmus-paper blue, and on treatment with sulphuric acid furnished sulphate of quinine.

To avoid the objection that might be made with regard to the action of the sulphuric acid on the lime-salts contained in the animal charcoal, I proceeded as follows:—500 grms. of the same bark were deprived of their soluble principles by repeated macerations in alcohol of 0·923, the resulting liquids filtered, the alcohol removed by distillation, the liquid residue mixed with two decoctions of the same bark in distilled water, the mixture filtered through paper, and then through animal charcoal which had been previously deprived of the salts of lime, &c. by hydrochloric acid, and well washed. The liquid passed slowly through the charcoal, and was deprived of its

bitter taste and colour. This charcoal was now washed, dried, and treated with alcohol of 0·848. The alcoholic solution left on distillation a mixture of quinine and resinous substance. To obviate this inconvenience, I repeated the preceding operation, adding to the mixture of the alcoholic macerations and aqueous decoctions a certain amount of acetate of lead, which precipitated the resinous substance. The liquid, filtered from this precipitate, and treated as above, furnished the quinine in a state of perfect purity.

These experiments, besides proving the pre-existence of certain alkaloids in plants, open a new path of organic analysis, and complete in some measure the study of the principal properties of animal charcoal.—*Ann. de Chim. et de Phys.*, September 1848.

On a new Modification of Phosphorus. By M. Schrœtter.

The author has found that the red substance formed upon the surface of phosphorus exposed to light, consists solely of an isomeric modification of the phosphorus. It takes place in gases, as hydrogen, nitrogen and carbonic acid, when the phosphorus is absolutely dry; it is consequently impossible to attribute the effect observed to oxidation. The metamorphosis is very active in direct light, but it is also perceptible with a faint diffuse light. Heat effects the same change. When phosphorus, previously well dried, is exposed for forty or sixty hours to a temperature between 464° and 482° F., the greater part is converted into phosphorus of a carmine-red colour. At first a red opake powder separates, but soon the change extends through the whole mass, which falls to the bottom of the vessel. M. Schrœtter has succeeded in completely converting phosphorus into the red modification by operating upon small quantities in a closed vessel, and prolonging the action under the conditions described.

The amorphous phosphorus may be isolated by means of sulphuret of carbon, which readily dissolves out the ordinary phosphorus, but scarcely acts upon the amorphous modification. It is collected upon a filter with certain precautions, and the residue then boiled with a solution of potash of 1·3 spec. grav., washed first with pure water, then with water containing a little nitric acid, and finally with pure water. Thus obtained, it forms a powder varying from a scarlet to a carmine-red. A brownish-black modification may be obtained under certain circumstances.

The density of the amorphous phosphorus was found to be 1·964 at 50°; it is lighter than melted ordinary phosphorus, and floats upon it. The author found 1·88 for the specific gravity of phosphorus melted at 113°, and 1·840 for solid phosphorus at 50°.

Amorphous phosphorus is not altered by exposure to the air; it is insoluble in æther, alcohol, naphtha, and in chloride of phosphorus; it dissolves sparingly in spirits of turpentine at an elevated temperature. It is far less combustible than ordinary phosphorus, and emits no light in darkness. It must be heated to 490° before it takes fire in the air. This is the temperature at which the

amorphous phosphorus begins to pass into the ordinary state when heated in an inert gas. It does not combine with sulphur at 234°, but requires heating up to 446°. It combines with chlorine without any disengagement of light. A boiling solution of potash acts upon the opake phosphorus, with disengagement of phosphuretted hydrogen, which is not spontaneously inflammable, but at the same time the phosphorus experiences a change; it is converted into the black modification described by Thenard. According to the author, phosphorus must first pass through the red state before conversion into the black modification.—*Comptes Rendus*, Oct. 23, 1848.

Observations on Caffeotannic Acid. *By* F. Rochleder.

Both Payen and Rochleder, in their investigations of coffee, have arrived at the same per-centage composition for caffeotannic acid. Payen however has assigned to it the formula $C^{14} H^{8} O^{7}$, and Rochleder the formula $C^{16} H^{9} O^{8}$. Both these formulæ, in fact, may be deduced from very accurately-corresponding per-centage numbers, as will be evident from the following:—

Carbon	14	=	56·8	16	= 56·8
Hydrogen	8		5·4	9	5·3
Oxygen	7		37·8	8	37·9

To decide which of these formulæ was correct, the author prepared some compounds of caffeotannic acid in a different manner to those he formerly described*, and has found that Payen's formula $C^{14} H^{8} O^{7}$ must be adopted.

Caffeotannate of Lead, $C^{42} H^{24} O^{21} + 5PbO$.—Dried and powdered coffee berries were exhausted with boiling alcohol of 0·912. The yellow filtered liquid was mixed while still hot with an alcoholic solution of acetate of lead, and the precipitate washed upon the filter with alcohol; upon this it was suspended in alcohol, decomposed with sulphuretted hydrogen, and the solution filtered from the sulphuret of lead, freed from sulphuretted hydrogen, and poured into a considerable amount of an alcoholic solution of acetate of lead; the yellow precipitate was washed with alcohol, and dried at 212°. It gave on analysis—

Carbon.....	25·00	42	= 3150·0	25·16
Hydrogen	2·25	24	300·0	2·39
Oxygen	16·89	21	2100·0	16·76
Oxide of lead ..	55·87	5	6972·6	55·69

Caffeotannate of Lead, $C^{42} H^{24} O^{21} + 4PbO$.—This second lead salt of caffeotannic acid was obtained in the following manner:—The dry and pounded coffee berries were exhausted in the cold with strong spirit, the filtered yellow solution precipitated with acetate of lead, the precipitate collected on a filter, decomposed with sulphuretted hydrogen, the liquid filtered from the sulphuret of lead, evaporated in the water-bath to the consistence of a syrup, mixed with

* Chem. Gaz., vol. v. p. 250 and p. 62 of the present volume.

absolute alcohol, decanted from the precipitate produced, filtered, the alcohol expelled by evaporation in the water-bath, the residue dissolved in water, and the turbid liquid, which passed milky through the filter, mixed with a few drops of a solution of acetate of lead, and filtered. The clear filtered liquid was poured into an excess of a boiling aqueous solution of acetate of lead, the precipitate, on cooling, collected on a filter, and washed with cold water. At 212° the yellow precipitate acquires a greenish tint; two analyses of this precipitate, made at different times, gave the following results:—

Carbon	28·15	28·49	42	= 3150	28·30
Hydrogen	2·53	2·63	24	300	1·69
Oxygen	18·65	19·37	21	2100	18·90
Oxide of lead ..	50·67	49·51	4	5578	50·11

These analyses agree with the formulæ contained in the author's former treatises, inasmuch as the composition of the organic substance, after deducting the oxide of lead or baryta, furnishes numbers which are intermediate between the formulæ $C^{14} H^8 O^7$ and $C^{14} H^6 O^5$. Their analysis proves that 2 equivs. of water are wholly or partially expelled from the caffeotannic acid, and replaced by oxide of lead. This would go to show that it is a bibasic acid, a view which is likewise confirmed by the caffeotannate of potash and theine, described by Payen. This also explains the difficulty of obtaining the combinations of caffeotannic acid with oxide of lead, free from traces of lime, magnesia or potash.

The composition of the acid $C^{14} H^8 O^7$ approaches very closely to the formula for catechine, $C^{14} H^7 O^7$; and the author has already, in a former treatise, drawn attention to the similarity of several of the reactions. Caffeotannic acid also contains as many equivalents of carbon as the kinic acid, $C^{14} H^{12} O^{12}$, derived from the family of the *Rubiaceæ*.

The production of viridic acid, $C^{14} H^7 O^8 = C^{14} H^6 O^7 + HO$, from caffeotannic acid is explained very simply by the assimilation of oxygen and elimination of 1 equiv. of hydrogen, $C^{14} H^8 O^7 + O^2 = C^{14} H^7 O^8 + HO$. The acids occurring in those plants which contain caffeine will therefore be—

Caffeotannic acid	= $C^{14} H^8 O^7$	= $(C^{14} H^6 O^5 + 2HO)$?
Viridic acid	= $C^{14} H^7 O^8$	= $C^{14} H^6 O^7 + HO$
Boheic acid	= $C^7 H^5 O^6$	= $C^7 H^5 O^6 + 2HO$

They may be regarded as oxides of a common radical, $C^7 H^3$, and their formulæ would then become $2(C^7 H^3) + O^5$; $2(C^7 H^3) + O^7$; $C^7 H^3 + O^4$.

As only in one case a salt of boheic acid could be obtained which corresponded to the formula $C^7 H^3 O^4$, PbO, and all the others contained 1 equiv. more water, it is possible that boheic acid must be expressed by the formula $C^7 H^4 O^5 + HO$, and not $C^7 H^3 O^4 + 2HO$. Caffeotannic acid would then be $2(C^7 H^4) + O^7$, and boheic acid $C^7 H^4 + O^5$.

Viridic and caffeotannic acids stand in the same relation to each other as salicylic and salicylous acids, and many others; caffeotannic acid might therefore also be called viridinous acid. Its properties of reducing silver from its salts, of absorbing oxygen, especially in the presence of bases, of acquiring a brown colour when combined with potash, soda, &c., and access of air, diffusing a peculiar odour, render caffeotannic acid the aldehyde of viridic acid.—Liebig's *Annalen*, lxvi, p. 35.

On Metallic Carbonates. *By* J. Lefort.

The author obtained the metallic carbonates which he examined by treating the salts with neutral alkaline carbonates and bicarbonates, both cold and hot.

Carbonate of Manganese obtained by the above methods is always represented by $CO^2+MnO+HO$. When heated it begins to lose water at about 194° F; it may be rendered perfectly anhydrous without any notable change of colour; it does not absorb oxygen below 576° F.; it is a white powder with a rose tint.

Carbonate of Cadmium.—Almost all treatises on Chemistry give CO^2+CdO as the formula of this compound; the author's analyses prove that it always contains 4 to 5 per cent. of water, or half an equivalent; this it loses between 180° and 248° F. Its composition is then $2CO^2+CdO+HO$.

Carbonate of Nickel.—Oxide of nickel forms three perfectly definite compounds with carbonic acid:—

1. A basic carbonate whenever cold solutions of the salts of nickel are precipitated by cold solutions of neutral carbonates. It is of an apple-green colour, and represented by $2CO^2+5NiO+8HO$.

2. A sesquibasic carbonate; the colour very nearly resembles that of the preceding; it is formed when the salts of nickel are treated with bicarbonates. Its formula is $2CO^2+3NiO+6HO$.

3. A pentabasic carbonate, which may be prepared by boiling the two preceding salts, or still better by precipitating the hot solutions of the salts of nickel by neutral carbonate of potash or soda. Its colour is meadow-green, and its formula $CO^2+5NiO+5HO$.

Carbonate of Chromium.—The salts of sesquioxide of chromium give with the alkaline carbonates and bicarbonates, sometimes a peculiar hydrate, and sometimes a definite compound represented by $CO^2+Cr^2O^3+4HO$. When sulphate of chromium of the green variety is treated with a neutral or alkaline bicarbonate, all the carbonic acid is disengaged, and hydrate of sesquioxide of chromium is at the same time precipitated; but if the operation be conducted with a salt of the violet blue modification, the salt formed is always that of the above-stated composition.

Carbonate of sesquioxide of chromium, exposed to the action of heat, loses at about 167° F., 19·58 per cent. of water, which corresponds to three equivalents; it does not lose its last equivalent of water and its carbonic acid till heated to above 572° F.

Carbonate of Bismuth exists in the anhydrous and hydrated state.

It is anhydrous whenever a salt of bismuth, as neutral as possible, is treated with an alkaline carbonate either cold or hot; no carbonic acid is evolved, and the precipitate formed has always the formula $CO^2 Bi^2 O^3$. But if instead of a neutral carbonate a bicarbonate is employed, much acid is disengaged, and a white precipitate, much lighter than the preceding, is obtained, represented by $CO^2 Bi^2 O^3 + HO$; it loses its equivalent of water at 212° to 248° F.

Carbonate of Lead.—Carbonate of lead obtained by treating a salt of lead with a neutral or bicarbonated alkali, possesses, as has been long known, the formula $CO^2 + PbO$; but when hot solutions are used, the composition is very different, and represented by $2CO^2 + 3PbO + HO$.

This composition is the same as that which MM. Mulder, Link and Hochstetter have found to exist in the different ceruses of commerce.

The author states that some comparative trials made by artists, have satisfied him that this new ceruse covers as well as those of the best manufactures in France, and it is less hurtful to workmen than the common operation.—*Comptes Rendus*, September 4, 1848.

On the Action of Sulphuretted Hydrogen upon the Nitryles. *By* A. Cahours.

When benzonitryle, obtained by distilling the benzoate of ammonia, is dissolved in alcohol rendered slightly ammoniacal, and a current of sulphuretted hydrogen passed into this liquid to excess, it soon acquires a brownish-yellow colour. If, at the end of some hours, the liquid is concentrated by boiling, and after having reduced it to about one-fourth of its volume water is added, a copious precipitate of sulphur-coloured flakes separates. This product dissolves entirely in boiling water, and is deposited, on very slow cooling, in long satiny needles of a sulphur-colour. The compound afforded on analysis the following results:—

Carbon	61·22	14	= 84	61·30
Hydrogen	5·13	7	7	5·11
Nitrogen	10·34	1	14	10·22
Sulphur	23·51	2	32	23·37

It is consequently sulphuretted benzamide.

When treated with binoxide of mercury, this substance is destroyed, water and sulphuret of mercury are produced, and benzonitryle regenerated. With potassium it affords sulphuret and cyanuret of potassium.—*Comptes Rendus*, August 28, 1848.

ANALYTICAL CHEMISTRY.

A few Remarks on the Processes of Reinsch *and* Marsh *for detecting Arsenic in Medico-legal Analyses.* *By* Dr. Douglas Maclagan.

Of these two processes, the former may be said to be distinguished for its facility and celerity, the latter for its delicacy. In any case

where there is reason to expect a considerable proportion of arsenic, and where we have plenty of material to work upon, it is always best to have recourse at once to Reinsch's method, on account of its easy and rapid execution. As I have frequently found, not only in experiment, but in actual medico-legal investigations, the whole process, including the preparation of a tube for the experiment, may be satisfactorily done in less than half an hour. Where, however, the quantity of material at command is small, and the proportion of arsenic probably minute, the more delicate method of Marsh ought to be employed at once. Reinsch's method cannot be said to be remarkably delicate. I have failed to obtain any satisfactory evidence of the presence of arsenic when it was applied to a thousandth of a grain in 2 fluid ounces of liquid. Dr. Christison says that it will detect "at least a 250,000th part of arsenic in solution;" but this applies to the state of dilution, without reference to the quantity of arsenic present. Mr. Taylor says it will act when a 3000th of a grain is used under a dilution of 90,000 times its weight of water; but the action in his experiments appears to have been limited to the mere production of a stain on the copper. This is acknowledged to be no true characteristic. The bright copper is frequently tarnished when there is no arsenic present, and where all the necessary precautions in conducting the experiment have been attended to. The circumstances which occasionally lead to the formation of a stain very like that of arsenic do not seem to be accurately determined. It will always almost occur in presence of organic matters, if the copper is put into the acidulated fluid before it is duly heated. Reinsch's process cannot be said to have acted satisfactorily for medico-legal purposes, unless it produces first a stain on the copper, and then a distinctly-recognizable white sublimate. It is, however, a method capable of demonstrating very small quantities of arsenic. Mr. Taylor detected the 144th of a grain in two fluid drachms of liquid. I have obtained all the indications of the presence of arsenic from 100th of a grain in 2 fluid ounces of thick soup.

The length of time during which the ebullition should be continued has been, I think, rather overstated both by Christison and Taylor. The former says (4th edition, p. 272), "In the feeblest solutions from ten to fifteen minutes elapse before arsenic is visibly deposited, and forty minutes should be allowed for complete deposition; but in strong solutions the action takes place in a few seconds." Mr. Taylor says (on Poisons, p. 353), "One caution is to be observed, *i. e.* not to remove the copper from the liquid too soon. When the arsenic is in minute quantity, the deposit does not take place sometimes for a quarter of an hour." As the amount of arsenic meant by the terms "feeblest" and "minute" has not been specified, I may mention an experiment bearing on this point, made with a definite quantity of arsenic, not however probably so small as to bring it strictly within either of these categories.

One-hundredth of a grain of arsenic in 2 fluid ounces of acidulated water was boiled in the usual way with a piece of copper. After having been boiled for four minutes, the copper was found to

have a slight gray crust, in eight minutes the crust was distinct, and in ten minutes the process was stopped. It was found, after this amount of boiling, not only that the copper afforded distinct evidence of arsenic, but that the whole had been removed, as none could be detected in the liquid by Marsh's method. A similar experiment, made with the same amount of arsenic in an equal quantity of thick broth, gave equally satisfactory results after ten minutes' boiling.

There does not appear however to be any practical disadvantage in prolonging the boiling. The mere coloration of the copper by the prolonged action of the acid is, as Mr. Taylor has accurately stated, not a source of fallacy, and the scaling off of deposited arsenic by prolonged ebullition has appeared to me to occur only when the arsenic was in large quantity; and in such a case the long boiling is not required. In any case where, after ten minutes' boiling, I find, on examining the copper, that it does not appear coated with arsenic, I remove the copper, boil the materials with the acid for some time longer, filter off the fluid, and transfer it to a Marsh's apparatus.

The peculiar form of the piece of copper, provided it be bright and clean, is not a matter to which I attach any importance. I give the preference to a piece of copper wire, of about the size called No. 24 by the dealers, made bright by rubbing it with a piece of sand-paper, and rolled into the form of a loose spiral coil, of about an inch long, by twisting it round a small pencil or glass rod. When of this form it is more easily caught and removed when it is immersed in a thick mixture of organic matter than a "slip of copper foil or wire" [Taylor], or "copper worn thin by the action of nitric acid" [Christison]. It affords, in a piece of moderate length, an extensive surface for the deposition of the arsenic, and thus expedites the process; and it is more readily washed and seen to be free from adhering organic matters than copper gauze. In operating by Reinsch's method, I never make any preliminary filtration of the decoction, but boil the whole solids, if any be present, broken down as much as possible, with the acid, adding water if necessary, and at once immerse the wire coil in the mixture.

Marsh's process is by universal consent the most delicate method of ascertaining the presence of arsenic. It is no part of my object to comment upon the innumerable forms of apparatus which have been devised. By far the most convenient is the common Döbereiner's lamp, as figured by Christison.

The purity of the acid, sulphuric or muriatic, and of the zinc and water, having been duly ascertained, and the stopcock and ground neck of the apparatus having been found by experiment to be air-tight, so as to avoid any risk of loss of the gas, the suspected materials are to be boiled in water along with a portion of acid, and filtered through a piece of well-washed calico. It is then quite fit, in almost every instance, for being placed in the apparatus. The proportion of acid should not be great—the slower the gas is evolved the better. It is convenient to set the process going at the end of the day, and leave it all night. The apparatus is found full of gas,

and ready for the decisive trial in the morning. The frothing up of the fluid, which has been such a bugbear to many experimenters, and has led to the troublesome and hazardous process of incineration, is productive of no practical inconvenience if this precaution is attended to.

The gas is now ready for being decomposed, so as to separate the arsenic. If the arsenic be in large quantity, it is of little consequence by what method the reduction of the arseniuretted hydrogen is accomplished. When the amount is minute, it is best to adopt the method first proposed by Berzelius, of passing the gas slowly along a small glass tube, raised at one part by a spirit-lamp to a low red heat, and thus obtaining a metallic ring, or more correctly incrustation, for it is seldom truly annular, in the interior of the tube.

In procuring stains on glass or porcelain, without considerable dexterity on the part of the operator, the quantity of arsenic, if very small, may be entirely lost; but in the use of the tube, if the gas is only passed along with moderate slowness, no loss can be experienced.

The most convenient tubes for this purpose are of German hard glass, about a twelfth of an inch in bore, and need not be more than 5 inches long. They are drawn out and turned up at the point, leaving in the apex a very small orifice, at which the disengaged hydrogen may be burned, and thus afford, by the size of the flame, a criterion of the rate at which the gas is passing. The reduction-tube is connected with the nozzle of the apparatus by a portion of wider tube about 2 inches long, filled with dry cotton-wadding, as recommended by Christison. The tube is to be heated at a little beyond its middle, till it appears feebly red when in shade. The tube, if of good glass, ought not to bend, and any tube which does so readily, or blackens when simply heated, from being made with lead, ought to be rejected. This method of operating, the simplification of which is due to Dr. Christison, is so simple, easy and sure, that all porcelain plates and watch-glasses, and the ingenious tube devised by Dr. Christison himself, for burning the gas and collecting the products of combustion, may be dispensed with.

It is however notorious, that the duty of the medico-legal analyst does not terminate with the procuring an incrustation on his tube or porcelain plate. What has been done is merely the elimination of something, the arsenical or non-arsenical nature of which remains to be determined.

Various matters have been indicated as being capable of producing deposits which may be mistaken for arsenical stains; but most medico-legal writers are now agreed that antimony is the only one which offers any really practical source of fallacy, and hence a variety of methods have been described for distinguishing with rigorous precision antimonial from arsenical stains.

When the metallic stain is large, this question is easily settled. Sublimation will in such a case yield enough of arsenious acid, if the deposit be arsenical, to afford precise characters by the liquid tests. But we may have to distinguish between arsenic and antimony,

where the quantity would not furnish enough of solution for testing with two or three separate reagents. The action of nitric or nitro-muriatic acid is that which has commonly been had recourse to for distinguishing stains of small extent. This, as is well known, converts the metallic arsenic into the very soluble arsenic acid, which gives a brick-red precipitate with nitrate of silver; whilst antimony so treated gives an insoluble product, and makes a gray stain with the silver test. But this proceeding is not easily applied except to stains on a flat surface; and in procuring these there is the risk of a considerable or total loss of the arsenic if the quantity be very minute and the operator not very dexterous. The most complete method of distinguishing arsenic from antimony is that of Devergie (Ann. d'Hygiène, xxxvi. 121), which may be applied to stains either in a tube or on a flat surface, and has the advantage, that the whole series of reactions may be applied to a single stain without the necessity for dividing it, for the purposes of experiment, into separate portions. This method consists in,—1st, exposing the deposit to chlorine gas, which causes the arsenical stain to disappear by converting it into chloride of arsenic; 2nd, the chloride so formed is exposed to sulphuretted hydrogen, which produces the pale yellow sulphuret of arsenic; 3rd, this is treated with a very weak *aqua ammoniæ*, which makes with it a colourless solution; and this, in its turn, being gently heated, reproduces the yellow sulphuret as the ammonia volatilizes; 4th, this yellow sulphuret is treated with a few drops of nitric, containing 1 drop of muriatic acid; and on evaporating this to dryness, white rings of arsenic acid are left, which, from their deliquescing under the moisture of the air, speedily become invisible; 5th, the spot moistened by the deliquesced arsenic acid is touched with nitrate of silver, which produces the dirty red stain of arseniate of silver.

This series of actions, if successfully evolved, is entirely conclusive for distinguishing a purely arsenical from a purely antimonial stain; but by M. Devergie's own showing, its success is a good deal dependent on the dexterity and nice manipulation of the operator. Devergie has, to a considerable extent, rebutted some of the objections which have been urged against his method. They are hardly valid where the stain is tolerably large; but he has given no positive statement as to the delicacy of his series of tests, or of how small a quantity of arsenic or antimony may be distinguished with certainty by its use.

There is one distinction between arsenic and antimony to which enough of attention has not been paid, and by which I believe they may be easily and readily discriminated even in very minute quantity, viz. the difference of temperature at which they respectively undergo sublimation. That such a difference exists is alluded to in general terms in most medico-legal works; but I am not aware that the comparative effects of a regulated temperature on the metallic stains have been adopted as a means of distinction, and adduced in evidence, except by Mr. H. H. Watson, in the case of the *Queen*

v. *Johnston*, Liverpool Lent Assizes, 1847. In the quotation of this evidence, as given by Mr. Taylor in his appendix, Mr. Watson says—"I also exposed some of these metallic deposits on glass, to a temperature ranging from 355° to 565°, by which they were volatilized and left the glass. This is another proof that the metal is not antimony, but arsenic; antimony does not volatilize at the temperature mentioned, but remains permanent, while it is one of the properties of arsenic to become volatilized at that temperature."

It appears to me that, when this property is satisfactorily observed, there can be no possible mistake as to the stain being arsenical, and not antimonial. Mr. Watson does not state how he applied and regulated the heat; but I presume that it was by the oil-bath. My experiments lead me to the conclusion, not only that it is the easiest and simplest way of distinguishing arsenic from antimony, but that it is a perfectly satisfactory method of separating them, and that they can thus be distinguished and separated in an unmistakeable manner whether the stain be large or small.

The exact point of the thermometer at which metallic arsenic and arsenious acid sublime is still *sub judice*. The arsenious acid is commonly stated to sublime at 380°; but, according to Dr. Mitchell of Philadelphia, it requires a temperature of 425°. My own observations lead me to fix on 380° as the temperature at which, in a narrow tube, open at one end, arsenious acid begins to sublime. The metallic arsenic, commonly said to sublime at 356°, does not, according to Mitchell, volatilize except at a low red heat, luminous in the dark. I have not made special experiments for determining this point; but I have never been able to observe it sublime below 500°, unless it became oxidated. In a medico-legal point of view, however, this is not the present question. What we have to consider is, if we can, by a simple means, obtain a regulated heat at which metallic arsenic will sublime and become oxidated, whilst antimony will undergo no such change.

This we can easily accomplish by means of a bath of olive oil, which may be urged even to its boiling-point without at all affecting an antimonial stain, whilst the heat so employed will entirely sublime an arsenical crust into a crystalline sublimate of arsenious acid. It will always be best, if it is possible, to have a thermometer in the oil-bath, that the extreme temperature employed may be stated in evidence if asked for. But this is not indispensable; olive oil does not begin to boil till the heat rises above 600°; and this heat, however long applied, does not cause antimony to volatilize. Stains which are so faint as not to appear distinctly metallic till the tube is held over a sheet of white paper, may be distinguished in this way. The pure arsenical metallic stain entirely disappears from the spot where it was deposited, the pure antimonial remains unchanged; whilst the mixed arsenical and antimonial becomes visibly less, a portion has undergone sublimation, whilst the residue, however long the heat may be prolonged, remains fixed. If, in addition to the disappearance of the stain from the portion of the tube immersed in

the oil, we can observe the formation of a crystalline sublimate in the upper portion of the tube, the proof may be said to be absolute. Very small quantities of arsenic may be rendered distinctly visible in this form. I have operated upon stains produced from a Marsh's apparatus, which contained less than a thousandth of a grain of arsenic, and have yet been able to see distinctly the crystalline character of the sublimate. The gentle and gradual way in which the heat is applied in the oil-bath causes the sublimate to deposit itself in fewer but much larger crystals, and thus makes it much more appreciable by the eye or lens than could be supposed by those who have been in the habit of subliming small stains of arsenic by a spirit-lamp flame. In the case of some poisoned swine which I examined, and where, from one of the articles, I could obtain in the tube a mere shade of brown, and when, by the spirit-lamp, this was sublimed into a mere white cloud, I was able, by again heating in the oil-bath, to obtain a sublimate distinctly of crystalline appearance to the naked eye.

In order to test practically the value of this method of distinguishing arsenic from antimony, I made the following experiment, in which I was kindly assisted by my colleague Dr. Anderson:—I requested him to prepare for me, in tubes, a series of stains from Marsh's apparatus, some of which should be arsenical, some antimonial, and others a mixture of both; and I proposed to distinguish these by the unaided operation of the oil-bath.

Dr. Anderson accordingly prepared for me six such tubes, which he duly numbered and noted.

No. 1 was accidentally mismanaged. Unreasonably trusting to my friend having taken the trouble to seal the tubes, I plunged this one into the oil with the point open, and it was of course filled with oil. Had such a misfortune occurred in a medico-legal investigation, it would have been easily rectified by immersing the tube in pure æther, which would dissolve out the oil; but as the crust in this case was large, probably the fiftieth of a grain, I felt so confident of success, that I contented myself with merely blowing out the oil from the tube, then sealed up the point, and again placed it in the oil. The distinct crystalline sublimate which speedily formed, showed at once that it was arsenical; and as it in time entirely volatilized, I pronounced against the presence of antimony.

Tube No. 2 presented a faint brown stain about two lines in length. Its brown metallic appearance was distinct only when it was held over white paper. It was pronounced to be arsenic alone, because it entirely disappeared; but it was so small as not to afford an unequivocally crystalline sublimate.

No. 3, on being heated for about ten minutes, presented at the upper part of the tube a faint crystalline sublimate, but a large metallic stain remained below. It was subjected to a prolonged heating, and no more sublimation could be observed. It was pronounced to be antimony with a small proportion of arsenic.

No. 4 gave a copious distinctly-crystalline sublimate in a few

minutes, and the whole stain eventually sublimed. It was recognised as a large arsenical stain, as in No. 1.

No. 5. The stain in this tube was so faint as to appear grayish-white when held to the light; but it was observed to have a faint brown tint when held over white paper. It was heated for a length of time, but underwent no apparent diminution. It was pronounced to be a trace of antimony.

No. 6, a large stain, was not affected by heating for above half an hour. It was evidently a large antimonial stain.

In each of these instances I found that I had pronounced correctly. The minute quantity distinguishable by these simple means may be inferred from this,—that in No. 5 the Döbereiner's lamp contained only three-thousandths of a grain of tartar-emetic; and as this salt contains only 35·9 per cent. of metallic antimony, there could not have been in the tube more than a thousandth of a grain of metallic antimony. But as only one charge of gas was used, it is most probable, from the faintness of the stain, that only a portion of this was collected. In order, therefore, to determine whether a stain be arsenical or antimonial, all that is required is to operate with Marsh's apparatus and the narrow glass tube; if a stain is procured, to seal up the point, immerse it in the oil-bath, and heat this steadily. The heating does not require to be prolonged. Ten minutes after the temperature has risen to about 500°, will have affected the stain if it is arsenical. It is well remarked by Taylor, that, in such investigations, we have to determine the presence of arsenic in antimony, not of antimony in arsenic; and therefore, if any sublimation in the oil-bath can be observed at all, the question as to the presence of arsenic is settled. To enable us to observe this more readily, it is a good plan to make a small scratch on the tube at each limit of the stained portion before heating it; and thus, by its diminution, we may pronounce upon its nature, although no sublimate should be distinctly visible. Should any peculiar case occur, in which it might be of importance to determine that antimony was present, as well as arsenic, the heat must be continued for a longer period. I have found that a large pure arsenical stain, weighing on a delicate balance 0·036 gr., required an hour and a half of heating at 500° in a narrow tube to sublime it entirely. But long before one-third had been sublimed, the tube was lined with splendid crystals of arsenious acid. The heat, to sublime the whole arsenic, need never be raised beyond 520°; but, even if the oil boils, it does not affect the correctness of the experiment.

I believe, therefore, from what I have been able to observe, that the nature of a metallic stain may in this way be accurately determined without the employment of any chemical reagent whatever. —*Edinburgh Monthly Journal*, November 1848.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Furfurol. *By* A. CAHOURS.

DÖBEREINER first observed, in the preparation of formic acid from starch, peroxide of manganese and weak sulphuric acid, the formation of a highly-volatile oil, which he called *artificial oil of ants*. Dr. Stenhouse subsequently obtained this product in greater abundance, by distilling a mixture of 2 parts of oatmeal, 2 parts of water, and 1 part of highly-concentrated sulphuric acid, until the products of distillation presented the odour of sulphurous acid. More recently Mr. Fownes obtained this same substance, to which he gave the name of furfurol (oil of bran), by distilling a mixture of bran and weak sulphuric acid. This process, which yields a much larger amount of oil than the other two, enabled that chemist to make a more complete examination of this interesting substance.

One of the most curious derivatives of furfurol is, without contradiction, that formed by the action of ammonia, and to which Mr. Fownes has given the name of furfuramide, to indicate the analogy it presents with hydrobenzamide. Messrs. Laurent and Gerhardt were led to conclude, from the low boiling-point of furfurol and the composition of furfuramide, that the equivalent of this oil ought to be reduced to the third of that assigned to it by Mr. Fownes, and that consequently the formula $C^{30}\,H^{12}\,O^{12}$, adopted by that chemist, should be replaced by the far more simple formula $C^{10}\,H^{4}\,O^{4}$. It was with a view to verify this assertion that I undertook the examination of this substance.

To prepare furfurol, I followed the method described by Mr. Fownes, but employed a somewhat smaller amount of sulphuric acid, and constantly obtained a much larger amount of furfurol than that chemist. With 6 kilogrms. of commercial bran, 5 kilogrms. of sulphuric acid of 1·834 and 12 quarts water I obtained 101 grms. of crude furfurol, and a liquid saturated with furfurol, which yielded by contact with ammonia 54 grms. of furfuramide, which is equivalent to 57 of furfurol, which makes altogether 158 grms. or 2·63 per cent., a quantity nearly three times as great as that obtained by Mr. Fownes. In a second experiment I obtained 2·52, and in a third 2·58 per cent.

Now which of the substances contained in the bran is decomposed

in the presence of sulphuric acid, and furnishes the furfurol? The latter certainly does not exist as such in the bran, of which I have convinced myself by distilling considerable quantities with pure water. Among the principles contained in bran are lignine, starch and gluten. I examined the action of sulphuric acid upon each of these products separately, but did not obtain the least trace of furfurol; the formation of this interesting oil therefore must be ascribed to some other principle contained in the bran.

Prepared according to the above directions, furfurol boils at 324° F., and presents all the properties ascribed to it by Mr. Fownes. On analysis it afforded the following results:—

Carbon.....	62·31	62·38	10 =	750	62·50
Hydrogen	4·29	4·23	4	50	4·17
Oxygen	33·40	33·39	4	400	33·33

which entirely agree with the results obtained by Mr. Fownes. In order to decide between the formula adopted by that chemist and the one proposed by Messrs. Laurent and Gerhardt, I took the density of the vapour of furfurol, and found 3·342 to 3·346; theory requires 3·349, supposing the formula $C^{10} H^4 O^4$ to represent an equivalent of the substance. The hypothesis of MM. Gerhardt and Laurent is therefore confirmed. Furfurol, from its behaviour towards ammonia, becomes homologous with the oil of Spiræa and the oil of bitter almonds; however, it is far from presenting, in its reactions with other bodies, results comparable with those which the above substances yield; thus, whilst chlorine and bromine furnish with the compounds of which the oil of bitter almonds is the type, derivatives which are either crystalline or volatile at fixed temperatures, and stand in a most simple relation to the primitive bodies, furfurol yields only black resinous substances. Nitric acid, both weak and concentrated, acts violently upon it, and affords as final product oxalic acid, instead of furnishing like those bodies, which belong to the aldehyde group, either an acid derived from furfurol by the simple fixation of oxygen, or a substance which differs only by the substitution of one or more equivalents of hyponitric vapour, or an equal number of equivalents of hydrogen. A mixture of sulphuric acid and peroxide of manganese, as also chromic acid, attack furfurol violently, and convert it into a brown substance. There are few products which yield, by their contact with furfurol, derivatives which stand in a simple relation to it as regards composition.

Of all the reagents ammonia is that which gives the best results; it is known, in fact, from the researches of Mr. Fownes, that furfurol becomes solid in contact with ammonia, yielding a crystalline substance analogous to hydrobenzamide, viz. furfuramide. This substance, when treated with a dilute solution of caustic potash, experiences a remarkable isomeric metamorphosis, yielding the alkaloid furfurine, which is analogous to quinine and morphine. I have prepared these different compounds, and have confirmed the perfect accuracy of the important results obtained by Mr. Fownes. I have

also procured some new compounds, which I shall now proceed to describe.

Furfuramide dissolved in alcohol is curiously acted upon by sulphuretted hydrogen; a compound is formed, which differs from furfurol in half the oxygen being replaced by sulphur. If the alcoholic solution is weak and the current of sulphuretted hydrogen very slow, a white crystalline powder separates after some time; if the solution is concentrated and hot and the current of sulphuretted hydrogen rapid, the substance separates with a resinous appearance. I have assured myself, by direct experiments, of the absence of nitrogen in this compound, which furnished on analysis—

Carbon	53·78	53·63	53·29	10	=750	53·58
Hydrogen	3·74	3·64	3·82	4	50	3·58
Sulphur	..	28·28	28·17	2	400	28·58
Oxygen	..	..	..	2	200	14·26

On account of the analogy of composition which this substance presents with furfurol, I propose to call it *thiofurfol.*

This product is also formed in the action of hydrosulphate of ammonia upon the solution of furfurol. Furfurine does not afford anything similar when a current of sulphuretted hydrogen is passed into its alcoholic solution for a very long time.

Seleniuretted hydrogen has a similar action upon an alcoholic solution of furfuramide; the clear liquid becomes turbid, and deposits a resinous substance, which furnished on analysis 38·05 carbon and 2·31 hydrogen. This substance consequently is analogous to thiofurfol, the 2 equivs. of sulphur being replaced by 2 equivs. selenium:—

Carbon	10	= 750·0	37·68
Hydrogen	4	50·0	2·51
Selenium.....	2	495·3	49·74
Oxygen	2	200·0	10·07

I have called it *seleniofurfol.*

When heated, thiofurfol melts, diffusing a strong disagreeable odour; if heated strongly in the air, it burns with a bluish slightly-smoky flame, diffusing a strong odour of sulphurous acid; on distillation it is entirely decomposed, producing a very beautiful crystalline substance, which no longer contains any sulphur.

This new substance, after being purified by crystallization from alcohol, forms long colourless or very faintly yellow needles, with an adamantine lustre. The crystals are hard, friable, and easily reduced to powder; it is insoluble in cold, sparingly soluble in boiling water, from which it separates on cooling in minute acicular crystals. It dissolves readily in alcohol, especially hot, and also in æther; its alcoholic solution is slowly changed by exposure to the air, acquiring a brown colour. Nitric acid acts violently upon it, and converts it into oxalic acid. On analysis it furnished—

Carbon.....	72·72	72·90	72·87	72·99	72·89
Hydrogen	5·31	5·24	5·36	5·20	5·23
Oxygen	21·81	21·86	21·77	21·81	21·88

The most simple formula which can be adopted to represent the composition of this product is $C^{18} H^{8} O^{4}$, which requires—

Carbon.....	18 =	1350	72·97
Hydrogen	8	100	5·40
Oxygen	4	400	21·73

For if we suppose the equivalent to be one-half less, we should obtain for the carbon an odd number of equivalents, which is not possible; but it may be that the preceding formula represents only a submultiple of the real equivalent; this question I have not been able to decide, not having succeeded in obtaining any well-defined combination of this substance or well-marked products of decomposition. The formula of thiofurfol can consequently not be $C^{10} H^{4} O^{2} S^{2}$; it must at least be doubled. The sulphuretted substances resulting from the action of hydrosulphuric acid upon the hydramides formed by the aldehydes must therefore possess a multiple equivalent of that of those aldehydes; unfortunately it is not possible to demonstrate the truth of this assertion in a direct manner, as all these products are decomposable by heat.

Nevertheless, it results from the facts observed by Mr. Fownes and myself, that furfurol belongs to that class of bodies which comprises the oil of bitter almond and of Spiræa. If I have not succeeded in producing derivatives analogous to those which the aldehydes usually form, it is owing to the instability of the molecule of furfurol when acted upon by somewhat energetic agents.—*Ann. de Chim. et de Phys.*, p. 277, Nov. 1848.

On the Salts of the Protoxide of Chromium. By A. Moberg.

The author brings forward a number of proofs to show that he had discovered the protochloride of chromium in the reduction of the perchloride by hydrogen earlier than Peligot, and had also made the observation, subsequently confirmed by Berzelius, that metallic chromium is mixed with the protochloride obtained in this manner. Moberg found, for instance, that when red anhydrous perchloride of chromium is heated to redness in dry hydrogen, the red colour is changed into a white one, and hydrochloric acid is given off; the composition however of this white substance and its solution were not perfectly established, as in the reduction a loss of 24·737 per cent. occurred, whilst theory requires only 22·164; and the residue consisted, after treatment with water, of soluble protochloride and oxide of chromium. The reason of this excess in loss was the employment of too high a temperature, the decomposition having proceeded too far. Part of the oxide of chromium obtained in this decomposition was already contained in the perchloride of chromium employed; another portion had been produced from the metallic chromium formed in the reduction; and it is also probable that the protochloride of chromium may have absorbed some oxygen from the dry air used to expel the hydrogen from the reduction-tube.

With respect to the protochloride of chromium, which was exa-

mined in solution, it was pure, as the analyses agree with the composition calculated with the atomic weight proposed by the author. They are also at least as accurate as Peligot's results; Moberg found 42·903, 43·630, 43·243, and Peligot 42·7, 42·0, 39·4 per cent. chromium; theory requires, according to the equivalent of chromium deduced by Moberg, 335·091, 43·05 per cent.

As Peligot has stated that Moberg made a mistake about the insoluble residue which the protochloride of chromium leaves, and ascribes its formation to the circumstance that the hydrogen employed by Moberg cannot have been free from oxygen, the author expressly states, that in all his subsequent experiments the hydrogen has been prepared from pure zinc and pure dilute sulphuric acid, and passed through a U-shaped tube, of which the first part was filled with fragments of glass moistened with a solution of acetate of lead, the second with caustic potash, and the third with protochloride of tin dissolved in caustic potash; it was then passed through a flask filled with pure concentrated sulphuric acid, and through a red-hot tube filled with red-hot copper, and lastly through a U-shaped tube containing fragments of chloride of calcium and caustic potash separated from each other by asbestos. Thus dried, the gas entered the straight tube which contained the perchloride of chromium. To be certain that no perchloride remained undecomposed, the temperature was raised higher than requisite for the reduction, the author having convinced himself that an admixture of metal did not influence the purity of the solution of the protochloride when the residue was separated from the solution. The property of the protochloride of chromium, and some other protochlorides, of rendering the insoluble modifications of the perchloride of chromium soluble, has been shown by Peligot and Pelouze. The author has also examined the action of the protochloride of chromium upon the same salt. Some perchloride was heated in a current of hydrogen to such an extent only, that scarcely a particle was converted into the white protochloride; on adding water which had been freed from air, the whole of the compound instantly dissolved. The dark green solution, concentrated over sulphuric acid, afforded acicular ramified crystals, and not granules as stated by Peligot; the crystals were of a light green colour and very deliquescent. As they could not be separated from the mother-liquor, the whole of the liquid was evaporated to crystallization, weighed in a covered dish, dissolved in water, and analysed by precipitating the oxide of chromium with ammonia, and the chlorine by nitrate of silver. The water was ascertained from the loss. The following results were obtained:—

Chlorine	39·405	6	39·699
Chromium	20·260	2	20·007
Water	40·335	12	40·294

These crystals differ consequently only in form, and not in composition, from those described by Peligot.

Those salts of the oxide of chromium which are almost insoluble in water, for instance the anhydrous neutral sulphate of the oxide of

chromium, and the sublimed perchloride of chromium, dissolve readily in water containing a little acid when a piece of zinc is inserted. The zinc is only affected by the free acid; consequently the solvent force and the re-arrangement of the atoms must apparently be ascribed to the reducing effect of those substances, without its being necessary to assume a successive reduction, as Lœwel has done.

Basic Protochloride of Chromium.—Ammonia produces in solutions of the protochloride of chromium a precipitate, which cannot be obtained free from ammonia by washing with water, on which account its composition could not be ascertained. In closed vessels the liquid retains its sky-blue colour, but when exposed to the air it is converted into the ammonio-chloride of chromium. The precipitate becomes green on exposure to the air, and dissolves with tolerable ease in muriatic acid, when hydrogen is disengaged, if the operation is conducted in closed vessels.

The Salts of the Protoxide of Chromium were prepared from the protochloride by dissolving it in water which had been freed from air, and precipitating with boiling solutions of salts of potash and soda. When precipitates were obtained, they were dried protected from the air.

A solution of bromide of potassium produces in the protochloride of chromium no precipitate; the colour of the liquid merely becomes of a somewhat darker green. The same reaction occurs with the iodide and the sulphocyanide of potassium. When these solutions are exposed to the air, they assume a brownish colour; that mixed with iodide of potassium deposits a yellow or bluish-green sediment. The fluoride of potassium precipitates a greenish powder, and the supernatant liquid becomes nearly colourless. No combination of the protoxide of chromium with sulphuric acid could be obtained; it was attempted in vain to dissolve the hydrated protoxide in sulphuric acid, or to precipitate the solution by sulphate of potash, soda, zinc or magnesia, or to decompose the solution of protochloride of chromium by sulphuric acid.

Sulphite of the Protoxide of Chromium.—The protochloride of chromium mixed with sulphite of potash furnishes a brick-red precipitate, which, washed with exclusion of the air, becomes chestnut-brown in a few days, and gradually bluish-green from the surface. It experiences this change very rapidly in the air, and is converted into the basic sulphite of the oxide of chromium.

Phosphate of the Protoxide of Chromium.—Phosphate of soda furnishes with the protochloride of chromium a copious blue precipitate, which dissolves readily in acids, and quickly turns green in the air.

Borate of the Protoxide of Chromium.—Borax produces a light blue precipitate, which is likewise the case with the neutral borate of soda; both dissolve in free acids, and are insoluble in an excess of the precipitant.

Carbonate of the Protoxide of Chromium.—The precipitate which is produced by a carbonated alkali resembles in many respects the

carbonates of magnesia, zinc and protoxide of iron; the protochloride, added to boiling solutions of carbonate of potash, produces a red or reddish precipitate, which, when the boiling is suddenly stopped, gradually assumes in the close vessel a bluish-green colour, whilst the liquid becomes yellow and deposits brownish-yellow scaly crystals, which on being placed upon bibulous paper become opake, turn green in the air, but still retain their lustre. They change to yellow in water, and furnish a yellow solution and a greenish-blue residue; but if more protochloride of chromium was added to the solution after it had cooled, sometimes a heavy yellow powder separated and a bluish-green flocculent precipitate, which appeared to originate from the former; for when the yellow powder was dissolved in water to a red liquid, the flocculent sediment gradually increased. On exposing the yellow or brownish-red liquid to the air, it turns green, depositing a greenish sediment, which is immediately precipitated by an addition of alcohol. When the liquid is placed in closed vessels, carbonic acid escapes, and the first greenish and flocculent precipitate is formed; this gives off carbonic acid and hydrogen, turns brown, and appears to pass into Peligot's hydrated oxide of the protoxide of chromium. The precipitate formed in the cold solution is not altered by boiling, except that it gives off carbonic acid, and now dissolves without effervescence in acids. The bicarbonate of potash behaves like the neutral salt, only that a greater amount of carbonic acid escapes with violent effervescence, and a larger portion of the protocarbonate of chromium is held in solution.

Oxalate of the Protoxide of Chromium is thrown down as a bluish-green precipitate from a solution of the protochloride by oxalate of potash; it appears to be for the greater part soluble in the deep bluish-green liquid.

Acetate of the Protoxide of Chromium, $CrO, C^4 H^3 O^3 + HO$, has been already prepared and examined by Peligot; it was obtained by mixing a hot solution of acetate of soda with a solution of protochloride of chromium. The liquid at first appeared red; but on cooling deposited red, shining, transparent, oblique rhombic prisms. When moist, these crystals very quickly change on exposure to the air, into a green powder soluble in water; in the dry state this takes place more slowly. They must therefore be kept in a vessel filled with carbonic acid. They dissolve readily in hot, sparingly in cold water, and furnished on analysis—

Carbon	25·045	4	25·347
Hydrogen	4·026	4	4·211
Oxygen	34·232	4	33·741
Protoxide of chromium	36·697	1	36·701

Formiate of the Protoxide of Chromium.—A solution of the protochloride of chromium is coloured of a beautiful dark blue by the formiate of soda, but does not deposit any crystals; and on evaporation *in vacuo* affords a green mass mixed with crystals of the chloride of sodium. It deposits a reddish-violet precipitate on being mixed over mercury with alcohol which has been boiled.

Citrate of the Protoxide of Chromium.—This is the least stable of all the salts of the protoxide of chromium; the violet-red precipitate instantly dissolves when heated, and more slowly in the cold, to a dark green liquid, whilst carbonic acid is disengaged.

Succinate of the Protoxide of Chromium, $CrO, C^4 H^2 O^3 + HO$.—The precipitate which is produced by succinate of soda in the protochloride of chromium is almost scarlet-red in the moist state; dried *in vacuo*, it becomes lighter, and at last partially blue, which colour it very quickly acquires in the air. According to analysis it consists of—

Carbon	25·254	25·488	4	25·616
Hydrogen	3·299	3·195	3	3·192
Oxygen	34·391	34·244	4	34·100
Protoxide of chromium	37·056	37·073	1	37·092

Benzoate of the Protoxide of Chromium, $CrO, C^{14} H^5 O^3$, is precipitated from a solution of the benzoate of potash by the protochloride of chromium, as a light grayish-red precipitate, which undergoes the same change as the preceding salt by exposure to the air. Dried *in vacuo* over sulphuric acid, or in a current of hydrogen at 212°, it lost at first water, and then became of a blue ash-gray. On analysis it furnished—

Carbon	56·027	14	56·873
Hydrogen	3·425	5	3·374
Oxygen	17·078	3	16·224
Protoxide of chromium	23·470	1	23·529

Moberg considers the atomic weight of chromium to be 335·091, which number has been employed in calculating the preceding results.

Reactions of the Salts of Chromium examined by the Author.

Neutral Perchloride of Chromium, $Cr^2 Cl^3$, exhibits at first no alteration on the addition of fluoride of potassium; it then becomes turbid, and subsequently furnishes a green precipitate; with borax and neutral borate of potash it gives a bluish-green; with phosphate of soda a green; with carbonate of soda a bluish-green, and with sulphuret of ammonium a green precipitate. No precipitate is produced by the bromide, iodide or sulphocyanide of potassium, sulphite, oxalate and bitartrate of potash, tartar-emetic, acetate and formiate of soda, citrate of potash and benzoate of potash. With the latter the liquid becomes coloured green after some time, with oxalate of potash violet, and with iodide of potassium reddish-brown.

Basic Perchloride of Chromium, $2Cr^2 Cl^3 + Cr^2 O^3$, furnishes the same precipitates as the preceding salt with fluoride of potassium, borax, neutral borate and phosphate of potash, sulphuret of ammonium and carbonate of soda. It gives with iodide of potassium a yellow; with tartar-emetic a light green; with benzoate of potash a bluish gray; with sulphite of potash a bluish-green precipitate; with succinate of soda a grayish-blue turbidness, and with bitartrate of potash a slight opacity, which is some time in making its appearance. It furnishes no precipitate with the other above-mentioned salts.

Chrome Alum furnishes with the phosphate of soda a dirty violet; with carbonate of soda a light bluish-gray; with benzoate of potash a grayish-blue crystalline precipitate, and with sulphuret of ammonium a green precipitate. The other reagents above-mentioned mostly colour the solutions of the salt green; sulphocyanide of potassium produces a red, and oxalate of potash a green colour, which subsequently changes to violet.

The Protochloride of Chromium, CrCl, furnishes with fluoride of potassium a light green precipitate; with bromide of potassium a dark green solution; with iodide of potassium no reaction; with sulphocyanide of potassium a dark green solution; with sulphite of potash a brick-red precipitate, which becomes brown-red in the course of a few days; with borax and with neutral borate of soda pale blue precipitates; with phosphate of soda a bright blue precipitate; with carbonate of soda a yellowish-green precipitate, and the liquid becomes yellow; with oxalate of potash a grayish-green precipitate, and the liquid becomes bluish-green; with bitartrate of potash no change; with tartar-emetic a green liquid; with acetate of soda a red liquid, which deposits red crystals; with formiate of soda a bright blue liquid; with citrate of potash a violet-red precipitate, which soon disappears after the evolution of some gas; with succinate of soda a scarlet precipitate; with benzoate of potash a light red precipitate, and with sulphuret of ammonium a black precipitate.—*Journ. für Prakt. Chem.*, vol. xliv. p. 322.

On the Oxidation of Dragon's Blood by Nitric Acid.
By H. Blumenau.

When the best dragon's blood in sticks is heated with from 6 to 8 parts nitric acid of 1·33 to 1·35, a most violent reaction occurs; red vapours are given off, the mass froths considerably, and at last actually boils, and does not become quiet or cool until the whole of the dragon's blood is dissolved and decomposed. The liquid is then perfectly clear. If a considerable excess of nitric acid has been employed, and the yellow liquid is now evaporated nearly to dryness, dissolved in water, and set aside to crystallize, *oxalic acid* is obtained, which is coloured yellow by a little colouring substance, or perhaps by a trace of nitropicric acid.

If, on the contrary, nitric acid of 1·33 to 1·35, mixed with an equal weight of water, is employed, a totally different result is obtained; the dragon's blood dissolves gradually at a gentle heat, with evolution of red fumes; the liquid which passes over smells strongly of nitrobenzide, or like prussic acid, and exhibits traces of an oily pellicle. It was frequently poured back into the retort until it contained but little nitric acid, then removed, and the residue in the retort again mixed with nitric acid, and distilled until the red fumes had almost entirely disappeared. The whole was then poured into a dish, evaporated nearly to dryness, set aside to cool, pressed between blotting-paper, and neutralized with carbonate of soda. The solution was decolorized with pure animal charcoal, then concen-

trated, and nitric acid added to it until it presented an acid reaction; the precipitate was collected on a filter, pressed, and washed with ice-water. It forms when dry a white mass of very minute scales, which consisted of two distinct substances, one volatile, the other not. The volatile acid sublimes, and crystallizes from water in the same form as benzoic acid; however, from the mode of its formation and its reactions, it cannot be this, but is Mulder's nitrobenzoic acid. It may be very easily separated from the fixed acid by a gentle heat. Of the latter acid I am unable, owing to an unfortunate accident, to say more than that it does not appear to crystallize readily, but usually separates as a powder, which at a high temperature turns brown and carbonizes.—Liebig's *Annalen*, July 1848, p. 127.

On some Isomorphous Double Salts of Chloride of Ammonium with Metallic Chlorides. *By* O. Hautz.

According to Pfaff, excess of ammonia precipitates half the magnesia from a solution of neutral muriate of magnesia. From the liquid filtered from this precipitate the author obtained the double chloride of ammonium and magnesium, $NH^4Cl, 2MgCl + 12HO$ (dried in the air), in large transparent prisms, belonging to the prismatic system. It is a very soluble salt. It corresponds to the double chloride of potassium and magnesium, $KCl, 2MgCl + 12HO$, which Marcet obtained by the careful evaporation of the mother-liquor of sea-water, and Liebig from the mother-liquor of the saline spring of Salzhausen.

This salt lost at 212° 10·9 per cent. = 4 equivs. water. Heated to 275°, the total loss amounted to 42·04 per cent. water. On analysis the following results were obtained:—

Ammonium	7·40	1	= 18·0	7·04
Magnesium	10·06	2	24·0	9·37
Chlorine	41·94	3	106·2	41·46
Water	42·04	12	108·0	42·13

Chloride of Ammonium and Nickel, $NH^4Cl, 2NiCl + 12HO$ (dried in the air).—This salt is very soluble in water and deliquescent in a moist atmosphere. It is obtained by saturating 2 parts by weight of muriatic acid with protoxide of nickel, and the addition of a liquid containing 1 part by weight of the same acid of the same degree of strength, saturated with solution of ammonia. When this liquid is concentrated, large green crystals separate in the course of a few days, which possess the same composition as the magnesium salt, and likewise belong to the prismatic system. Prepared according to the method described by Tupputi, stellate twin crystals are obtained, consisting of aggregation of tetrahedrons; their analysis however showed, according as they were of a lighter or darker colour, small variable quantities of chloride of nickel. The salt, heated gradually to 275°, lost 37·86 per cent. of water. The analysis of the air-dried salt gave—

Ammonium	..	1 =	18·0	6·17
Nickel	20·05	2	59·2	20·31
Chlorine	36·44	3	106·2	36·44
Water	37·86	12	108·0	37·08

Chloride of Ammonium and Cobalt, $NH^4Cl, 2CoCl + 12HO$ (dried in the air), is a beautiful ruby-red deliquescent salt, which dissolves readily in water. It is formed by mixing solutions of protoxide of cobalt in 2 parts of muriatic acid, and of ammonia in 1 part of the same acid; the crystals belong to the prismatic system. They lost at 275° 38·5 per cent. of water, and gave on analysis—

Ammonium	6·50	1 =	18·0	6·18
Cobalt	20·31	2	59·0	20·26
Chlorine	36·16	3	106·2	36·46
Water	38·50	12	108·0	38·50

The three following salts also belong to the prismatic system, and part with 3 equivs. water at 212°:—

Chloride of Ammonium and Manganese, $NH^4Cl, 2MnCl + 4HO$ (dried in the air).—If, as in the case of the preceding salts, solutions of 1 equiv. of chloride of ammonium and 2 equivs. of protochloride of manganese are mixed and concentrated, this double salt separates in pale red crystals, which dissolve in one-half part water at the ordinary temperature, and part with 13·9 per cent., or 3 equivs. water, at 212°. The air-dried salt furnished on analysis—

Ammonium	..	1 =	18·0	9·84
Manganese	28·69	2	56·0	29·54
Chlorine	55·52	3	106·2	55·76
Water	4·09	1	9·0	4·86

Chloride of Ammonium and Zinc, $NH^4Cl, 2ZnCl + 4HO$.—This salt, which is perfectly analogous to the manganese salt just described, was obtained from a mixture of 1 part of chloride of ammonium with 2 parts of protochloride of zinc; it crystallizes in the same form, is far more soluble, and almost deliquescent. Up to 275° it parts with 16·26 per cent. water. Analysis gave—

Ammonium	8·00	1 =	18·0	7·95
Zinc	29·05	2	66·0	29·17
Chlorine	46·46	3	106·2	46·95
Water	16·26	4	36·0	15·93

Chloride of Ammonium and Copper, $NH^4Cl, 2CuCl + 4HO$ (dried in the air), obtained by saturating 1 part of muriatic acid with ammonia, and 2 parts of the same acid with carbonate of copper, and mixing the two solutions. It forms beautiful bluish-green crystals, which dissolve in 2 parts of water. They furnished on analysis—

Ammonium	8·08	1 =	18·0	8·05
Copper	27·79	2	63·4	28·30
Chlorine	47·39	3	106·2	47·49
Water	16·46	4	36·0	16·16

No similar compound could be obtained with iron or chromium.

Ammonio-chloride of Zinc, $NH^4Cl + ZnCl + HO$, crystallizes in large shining laminæ, and dissolves in $\frac{1}{2}$ part water. It was obtained once on mixing 2 equivs. muriatic acid with 1 equiv. carbonate of zinc, then adding 1 equiv. muriatic acid, saturating the solution with ammonia and evaporating. It gave on analysis—

Ammonium	..	1 =	18·0	13·76
Zinc	25·16	1	33·0	25·23
Chlorine	54·90	2	70·8	54·13
Water	7·40	1	9·0	6·88

Ann. der Chem. und Pharm., lxvi. p. 280.

Observations on Nitropicric Acid. By H. Blumenau.

In most works on chemistry it is stated that nitropicric acid is not decomposed by nitric acid; but that this acid is really decomposed under certain circumstances, and apparently into nitric oxide, oxalic acid, and probably also carbonic acid, appears to be little known. The following brief notice upon this subject, and on some other points connected with nitropicric acid, may probably interest the reader.

In preparing some nitropicric acid, 3 lbs. of the best indigo were conveyed into 35 lbs. of nitric acid just upon the boil; and as soon as the violent action had ceased, transferred into a retort. A very considerable quantity of so-called resin had formed, but the liquid furnished on cooling an abundant crop of crystals. To destroy the resin, the contents of the retort were kept ten hours a day for a week on a gentle boil. There was a constant evolution of red vapours, and the resin, with the exception of a mere trace, had disappeared; but now the inspissated liquids furnished a very small crop of crystals of nitropicric acid, which latter, instead of amounting at least to 12 oz., scarcely weighed 6 drms. As the whole operation was very carefully conducted, I can only ascribe the disappearance of the nitropicric acid to its decomposition by the nitric acid. In a subsequent investigation, in which the heat was applied but for a short time, the produce constantly amounted to one-fourth of the indigo employed, proving consequently that a decomposition of the nitropicric acid must have taken place in the first experiment.

Nitropicric acid varies considerably in the form of its crystals; from boiling water I obtained it in lemon- or canary-yellow coloured, thin, *opake* laminæ of the known form; by exposure to warm air these laminæ became *transparent*, and now exhibited a yellowish-brown colour. The acid crystallized from alcohol was of the same form, and possessed the same transparency and colour. From æther the acid crystallizes, on slow evaporation, in very beautiful yellowish-brown transparent crystals, with a faint vitreous lustre, and in the form described and measured by Mitscherlich. By long exposure to the air these crystals acquire externally the colour of the laminæ which had separated from hot water. By breathing upon these yellow and dull crystals, they again become

transparent, and brown if the decomposition has not penetrated too far into the interior. It appears consequently as if the transparency were produced in the crystals which have separated from water by a loss of water, whilst the same cause determines the opacity in those crystals obtained from æther.—Liebig's *Annalen*, July 1848, p. 115.

On Liquid Protoxide of Nitrogen. *By* M. Dumas.

M. Natterer of Vienna has constructed a forcing-pump for the liquefaction of gases, by means of which carbonic acid and protoxide of nitrogen can readily be obtained in the liquid state. Having procured one of these instruments, and employed it more especially for the liquefaction of the protoxide of nitrogen, I soon perceived the necessity of using a series of indispensable precautions, but which, once adopted, have enabled me to effect with promptitude and security, as well as œconomy, the liquefaction of large quantities of protoxide of nitrogen.

As this liquid furnishes a means of producing an excessively low temperature, and is very easily handled, I will here briefly point out the observations I have made. The first relates to the principal piece of the apparatus, that is to say the reservoir. In my opinion the Viennese manufacturer has not given it sufficient strength. I have had it surrounded with a belt of forged iron, capable of resisting 800 atmospheres, and very nicely made by M. Bianchi. Moreover, I arranged things so that the reservoir being surrounded by ice, the body of the pump was cooled uninterruptedly by a circulation of water around it, and that even the stem of the piston was always moistened by cold water; in this manner there is no danger of the valve of the piston being injured by the heat proceeding from the compressed gas, and by its special action as a combustible gas. With these precautions, we may compress into the reservoir in the course of two hours 200 litres of gas, of which 20 suffice to produce a pressure of 30 atmospheres, about which liquefaction commences. The remainder of the gas furnishes a liquid; 100 litres yield 200 grms., or very nearly. The gas should be absolutely dry in order to succeed, and likewise as pure as possible. I prepare it from the nitrate of ammonia as usual, and after having dried it, pass it into Macintosh bags; a couple of pounds of nitrate of ammonia suffices.

Once compressed, the liquid gas may be preserved for one or two days at least in the reservoir; the valve however is slightly injured by it. When the stopcock of the reservoir is opened, the gas escapes; a portion freezes at first, but it then flows liquid; the solid portion resembles a mass of snow; it melts upon the hand, and rapidly evaporates, leaving a severe burn. The liquid portion, which is by far the most abundant, and of which it is easy to obtain in one operation 40 to 50 grms., being received in a glass, keeps for half an hour, or even more, in the air.

In order to observe more readily its properties, I collected it in open tubes, contained in vessels at the bottom of which was placed

some pumice-stone moistened with sulphuric acid. It then retains its transparency for a very long time.

The protoxide of nitrogen is liquid, colourless, very mobile and perfectly transparent; each drop that falls upon the skin produces a very painful burn. The gas, which is incessantly liberated by a slow ebullition, possesses all the properties of the protoxide of hydrogen. When metals are dropped into this liquid, they produce a noise like that of red-hot iron immersed in water. Quicksilver causes the same noise, instantly freezes, and affords a hard brittle mass, white like silver, which it perfectly resembles in appearance. Potassium floats upon the liquid, and experiences no change; the same is the case with charcoal, sulphur, phosphorus and iodine. Ignited charcoal floats upon the surface of the liquid, and burns with considerable brilliancy, and frequently until the whole is consumed. Ordinary sulphuric acid and concentrated nitric acid freeze immediately. Æther and alcohol mix with the liquid without freezing. Water is instantly converted into ice; but it produces such a sudden evaporation of a portion of the liquid, that it causes suddenly a kind of explosion, which would be dangerous if merely a few grammes of water were poured at once into the liquid.—*Comptes Rendus*, Nov. 6, 1848.

On the Action of Fuming Nitric Acid and of a Mixture of Sulphuric and Nitric Acid upon the Salicylate of Methylene and Anisic Acid. *By* A. Cahours.

In my researches upon the action of a mixture of fuming sulphuric and nitric acids upon organic substances*, I showed that the salicylate of methylene, under the influence of this reagent, exchanged 2 equivs. of hydrogen for 2 equivs. of hyponitric vapour, and furnished the binitro-salicylate of methylene, $C^{16} H^6 O^6, 2NO^4$.

When treated with a boiling concentrated solution of potash, this product is decomposed into a potash salt, which separates in acicular crystals of a magnificent crimson colour. If dilute nitric acid is poured into a concentrated solution of the latter, a yellow powder separates, which dissolves in boiling water, from which it separates on cooling in the form of a beautiful yellow crystalline powder. This product, the true nature of which I at first mistook, considering it to be the free acid of the preceding salt, is a salt of potash, which can only be deprived of its base by the most powerful and concentrated acids, such as sulphuric acid, behaving in the same manner as the bichlorinated and bibromated salicylic acids, which also form very stable, slightly soluble salts, that are only decomposed by strong acids. Several analyses of this substance and of some of its salts have shown that its composition should be represented by the formula $C^{14} H^4 O^6, 2NO^4$. It differs from salicylic acid, $C^{14} H^6 O^6$, in 2 equivs. hydrogen being replaced by 2 equivs. hyponitric vapour. This acid, which is nearly insoluble in cold, dissolves readily in

* Chem. Gaz., vol. v. p. 213.

boiling water, and separates on cooling in the form of long white needles with a faint tint of yellow, analogous to caffeine. By spontaneous evaporation it sometimes crystallizes in short prisms grouped around a common centre. It dissolves readily in alcohol and æther, and separates in a crystalline state on evaporation.

When a current of hydrochloric gas is passed into an alcoholic solution of this acid at a temperature of 158° to 176°, it is soon converted into æther; water added to the alcoholic liquid reduced to half its bulk, precipitates a heavy yellowish oil, which soon solidifies. This product, purified by one or two crystallizations from alcohol or æther, forms very brilliant yellowish-white laminæ, which have a great resemblance to the binitro-salicylate of methylene. Several analyses of this substance have led to the formula $C^{18} H^8 O^6, 2NO^4 = C^{14} H^3 N^2 O^{13}, C^4 H^5 O$.

It may also be obtained by treating salicylic æther with a mixture of fuming sulphuric and nitric acids.

Anisic acid, which is isomeric with the salicylate of methylene, furnishes very different products when acted upon either by fuming nitric acid or a mixture of this acid and Nordhausen sulphuric acid. When treated with fuming nitric acid at a gentle heat for some minutes, anisic acid exchanges 1 equiv. hydrogen for NO^4, furnishing nitranisic acid, which is isomeric with the indigotate of methylene. If, instead of operating thus, the anisic acid is boiled for half an hour with from 8 to 10 times its weight of fuming nitric acid, a perfectly neutral product is obtained, which is insoluble in water, crystallizes in long needles, and presents the composition and properties of binitro-anisol, $C^{14} H^6 O^2, 2NO^4$.

When treated with a mixture of fuming sulphuric and nitric acids at a boiling heat, anisic acid furnishes a perfectly neutral product, like the preceding, which I had erroneously considered to be the trinitro-anisic acid. This substance, which crystallizes in beautiful rhomboidal tablets of considerable size, is the trinitro-anisol, $C^{14} H^5 O^2, 3NO^4$. Such is undoubtedly the constitution of these two compounds, for they may be obtained with the same properties by acting with the same reagents upon anisol.

I have ascertained that when these products are formed there is at the same time disengaged a considerable quantity of carbonic acid. These reactions may therefore be expressed by means of the following equations:—

$$C^{16} H^8 O^6 + 2NO^5, HO = 2CO^2 + 4HO + C^{14} H^6 O^2, 2NO^4.$$
$$C^{16} H^8 O^6 + 3NO^5, HO = 2CO^2 + 6HO + C^{14} H^5 O^2, 3NO^4.$$

Both the binitro-anisol and trinitro-anisol, when treated with a concentrated solution of potash, are decomposed, the first into nitrophenesate, the second into nitrophenisate (picrate) of potash.

$$C^{14} H^6 O^2, 2NO^4 + KO, HO = C^{12} H^3 N^2 O^9, KO + C^2 H^3 O, HO.$$
$$C^{14} H^5 O^2, 3NO^4 + KO, HO = C^{12} H^2 N^3 O^{13}, KO + C^2 H^3 O, HO.$$

According to this, anisol would be a true æther, the phenate of methylene; binitro-anisol would be nitrophenesate, and trinitro-anisol the nitrophenisate.

Salicylate of methylene is represented by the formula $C^{14} H^{5} O^{5}$, $C^{2} H^{3} O$. Under the influence of anhydrous alkalies, salicylic acid loses two molecules of carbonic acid, and is converted into phenyle, which in the nascent state remains combined with the oxide of methyle, constituting the phenate of methylene or anisol.

In the same manner salicylic æther, when treated with anhydrous alkalies, loses two molecules of carbonic acid, and is converted into a neutral product, phenetol, the homologue of anisol, $C^{16} H^{10} O^{2} = C^{12} H^{5} O, C^{4} H^{5} O$, which I look upon as phenic æther.—*Comptes Rendus*, Nov. 6, 1848.

ANALYTICAL CHEMISTRY.

On a new Method for the Detection of the principal Metallic Poisons. By M. Abreu.

The want of a positive method must frequently have been regretted by persons called upon to examine in cases of poisoning. The various treatises on poisons, which contain so many valuable details respecting the mode of examination for poisons, leave the reader in the most serious embarrassment, by proposing for each poison different processes, which are far from presenting the same value, and the best of which are frequently very dissimilar, for the different poisons. This gives rise to a serious inconvenience; for to ascertain the presence of any suspected substance, it is requisite to make as many experiments, to analyse separately as many parts of the substance as suppositions may be entertained, if the problem does not consist in the detection of a certain poison.

We have endeavoured to supply this want as regards the different metallic poisons, and to reduce the medico-chemical operations to a simple problem of analytical chemistry,—*Determine the nature of one or several metals mixed up with organic matter.* To solve this important problem, we have successively passed in review the several methods hitherto proposed for the special detection of each metal. Our method will comprise the compounds of the following metals:—

Arsenic.	Mercury.	Tin.
	Copper.	Zinc.
Antimony.	Lead.	Silver.

The following is the plan of operation:—The experimenter should begin by examining attentively with a lens the substances vomited and evacuated, those found in the digestive canal, and the mucous surface of this canal. This will frequently furnish valuable indications; and in some cases it is possible to find in the digestive canal, especially in its mucous folds, solid particles of the poisonous substance. In this latter case the particles of poison should be carefully removed with a small forceps, and their nature ascertained if possible by the ordinary methods; but supposing no definite result to follow

from this physical examination, we proceed as follows:—The suspected matter to be examined is cut into small pieces with a pair of very small scissors; and a known weight of it, which should never exceed 200 grms., conveyed into a flask capable of holding 2 quarts, with half its weight of pure fuming muriatic acid. A cork with two perforations is adapted to the neck of this flask, into one of which is fitted a tube from 55 to 60 centimetres in length and 1 centimetre internal diameter. It dips a few millimetres into the muriatic acid. The second perforation is destined for a tube curved at right angles, the second vertical branch of which passes through a cork into some distilled water contained in a test-tube; this cork has also a second perforation, into which is fitted a straight tube not dipping into the water. When this arrangement is made, the flask is placed on a sand-bath, and the test-tube immersed in cold water, which is changed from time to time. The sand is kept at a temperature near the boiling-point of the liquid, and the flask is agitated from time to time for at least four hours. The organic matter is gradually disintegrated, and finally forms a dense homogeneous liquid of a more or less dark colour. The flask is then removed from the sand-bath, and boiled over an Argand lamp for two or three minutes, upon which some crystals of chlorate of potash are gradually introduced through the large tube, taking care to agitate the flask constantly until from 16 to 18 grms. have been used for every 100 grms. of suspected substance employed. A violent reaction takes place, with an abundant disengagement of chlorinated gases; the liquid gradually clears, and at last becomes perfectly transparent and of a yellow colour, the intensity of which appears to depend especially on the large excess of chlorine remaining in solution. Both the liquid in the flask and the water in the test-tube present the peculiar odour of chlorine in the highest degree. Some small fragments of charcoal and of a resinous substance float upon the liquid in the flask; their quantity is very small in investigations of blood, but very considerable in examinations of the tissues of the liver and other parenchymatous organs.

The apparatus is allowed to cool, the liquid in the flask filtered through Swedish paper, and mixed with the water in the test-tube and with the wash-waters. A current of well-washed sulphuretted hydrogen is passed through the united liquids for a considerable time, and the whole is then left till the morning in a corked flask. In all cases there will be a more or less abundant precipitate, which should be examined for all the metals comprised in our table except silver and zinc. This precipitate may nevertheless contain only sulphur and a little organic substance, which should be got rid of by the following plan:—

The precipitate is thrown upon a filter without folds, washed with distilled water, and boiled in a small flask with its weight of pure and fuming muriatic acid, to which a few fragments of chlorate of potash are added. When the reaction is complete, a little distilled water is added, and the whole heated with great care, in order to expel the whole of the free chlorine. It is again filtered through

Swedish paper, and a very transparent liquid is thus obtained with but a faint tint of yellow. The arsenic, antimony, mercury, copper, lead and tin, if the suspected matter contained any, will have to be sought for in this liquid. As zinc is not precipitated by sulphuretted hydrogen from an acid solution, it must be sought for in the liquid obtained by filtration after the action of the sulphuretted hydrogen. The silver will be found in the residue from the first filtration.

The numerous experiments which we have made prove the advantage of this method; some were made upon 2 milligrms. of poisonous substance, mixed with large quantities of animal substances.—*Journ. de Pharm.*, Oct. 1848, p. 241.

CHEMICAL PREPARATIONS.

Prescribed Forms for the Sale of Arsenic in France.

According to the laws of France, the sale of arsenic and its compounds, for other than medicinal purposes, is prohibited unless mixed with other substances.

The following forms recommended by the professors of the *Ecole Nationale Vétérinaire* of Alfort, and by the *Ecole de Pharmacie*, have been approved of by the Minister for Agriculture and Commerce:—

Arsenical Paste for the Destruction of Vermin.

℞	Of melted suet	1000 parts.
	Of wheat flour	1000 ...
	Of arsenious acid in very fine powder	100 ...
	Of lamp-black	10 ...
	Of oil of aniseed	1 ...

Melt the suet in a pipkin over a gentle fire, then add the other substances, and mix accurately.

This preparation may be employed for the destruction of vermin, either alone or mixed with an equal part of bread-crumb, or any other substance which attracts the animals required to be destroyed.

Arsenical Soap for the Preservation of the Skins of Animals.

℞	Pulverized arsenious acid	320 parts.
	Dried carbonate of potash	120 ...
	Distilled water	320 ...
	Mottled Marseilles soap	320 ...
	Quicklime in fine powder	40 ...
	Camphor	10 ...

Place the water, arsenious acid and dry carbonate of potash in a porcelain capsule capable of holding three times their amount; ap-

ply heat, stirring frequently to facilitate the disengagement of the carbonic acid. Continue the application of the heat, and boil gently until the arsenious acid is completely dissolved, then add the soap finely broken up, and withdraw the heat.

When the soap is dissolved, add the powdered lime and the camphor reduced to powder by means of alcohol. Lastly, mix well on a marble slab, and put the compound into a closed pot or corked wide-mouthed bottle.

Preparations used in Veterinary Surgery.

For External Application.

1. *Powder for* Tessier's *Bath.*

Arsenious acid	2 parts.
Protosulphate of iron	20 ...
Anhydrous protoxide of iron (colcothar)	800 ...
Gentian root in powder	400 ...

Triturate the arsenious acid and the protosulphate of iron separately in a mortar, then mix the two substances intimately, add the protoxide of iron and the powdered gentian root, and again mix well. Preserve this compound powder in glass vessels well corked.

2. Tessier's *Bath.*

Powder for the bath (No. 1.)	11 kilogrms. 600 grms.
Water	100 litres.

Place the powder in a large cast-iron pot with the 100 litres of water, boil until the mixture is reduced to a third, replace the water lost by evaporation, or 66 litres, allow it to boil for eight or ten minutes, withdraw the fire, and pour it into a tub for the bath.

3. Tessier's *Lotion.*

Powder for Tessier's bath (No. 1.)	1 kilogrm.
Water	10 litres.

Place the powder in an iron pot with the 10 litres of water, boil down to a third, replace the water lost by evaporation, or 6 litres, boil for eight or ten minutes, withdraw the fire, and pour it into a vessel to wash the diseased parts.

Caustic Preparations.

4. *Caustic Powder modified from* Côme's *Formula.*

Arsenious acid	10 grms.
Bisulphuret of mercury (vermilion)	60 grms.
Dragon's blood	1 grm. 2 decigrms.

Separately reduce the three substances to very fine powder, then triturate them until they are intimately mixed. The caustic action of this powder may be increased by the addition of a larger propor-

tion of arsenious acid. It may be diminished by augmenting that of the bisulphuret of mercury and the dragon's blood. When mixed with gum-water, this powder or caustic may be used to make caustic pastes.

5. Catharetic Powder.

Finely-powdered arsenious acid	4 parts.
Red sulphuret of mercury.....	2 ...
Lard	32 ...

Thoroughly incorporate the arsenious acid and the red sulphuret with the lard in a porcelain mortar.

Arsenical Preparation for Internal Use.

6. Fowler's *Solution.*

Arsenious acid.....	5 parts.
Carbonate of potash	5 ...
Water	500 ...

Reduce the arsenious acid to powder, as also the carbonate of potash, boil in a glass vessel until the arsenious acid is completely dissolved, filter and keep in a well-stopped bottle. Add to this liquid, at the time of its delivery for use, the following solution:—

Powder of gentian root (*Gentiana lutea*)	4 parts.
Water	250 ...

Boil the gentian powder in the water for twenty minutes. Add this decoction to the quantity of Fowler's solution above prescribed, so as to impart to it a very bitter taste.—*Journ. de Pharm.*, Sept. 1848.

Pate Dépilatoire.

This paste is prepared by suspending lime in water in a tubulated bottle, and passing sulphuretted hydrogen into it until no further absorption of gas takes place. The lime assumes a greenish-gray tint, and quickly subsides. It is employed in the form of a paste. As it exhales a strong odour of sulphuretted hydrogen, its use should be avoided in those parts situated near the organs of respiration.

This preparation, which has been described as new by M. Böttger, is the depilator of Martius, described by M. Dorvault in the 'Officine.' It is spread in a tolerably thick layer over the part to be deprived of hair, and removed after twelve to fifteen minutes with a moist sponge, which at the same time carries away the hairs which have been separated at their entrance into the canal which they traverse before reaching the bulb.

The only inconvenience with this paste is its odour, which prevents its being used on the face, especially near the nose or mouth. In other respects it is far preferable to all other depilatory preparations which contain arsenic or mercury.—*Journ. de Pharm.*, Oct. 1848, p. 281.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Absorption of Carbonic Acid Gas by Sulphuric Acid. *By* Prof. W. B. Rogers *and* Prof. R. E. Rogers *of the University of Virginia*.*

In a memoir on the absorption of carbonic acid gas by liquids, read before the American Association of Geologists and Naturalists in September last, and of which an abstract was given in the January number of the American Journal of Science, we called the attention of chemists to the fact, disclosed we believe for the first time by our experiments, that sulphuric acid of the common density is capable, under ordinary pressure, of absorbing about 94 per cent. of its volume of dry carbonic acid gas. We at the same time adverted to the effect of this property of sulphuric acid in impairing the accuracy of the various important researches in which atmospheric air, and other gaseous mixtures containing CO^2, are made to pass through or over a considerable volume of the acid preparatory to their analysis.

This large absorption, amounting to more than twice the effect stated by Saussure, is only to be attained by a brisk and continued agitation of the liquid in an atmosphere of CO^2 of unvarying tension. By means of the apparatus described and figured in the July number of the 'American Journal of Science,' we find it easy to effect the absorption completely in about twenty minutes. The results thus obtained in numerous trials rarely differ as much as a half per cent. The accuracy of our determinations with this apparatus will we think not be questioned by those who examine the process of experimenting detailed in our memoir, or who will be at the trouble of repeating the experiments with the precautions we have used. As, however, the observations published in some recent numbers of the 'Chemical Gazette' might lead to the inference that the results announced by us were erroneous, and that sulphuric acid *does not* possess the great absorbent power we have claimed for it, we ask the attention of chemists to the following notes of various simple experiments, which, without furnishing accurate quantitative results, will suffice to show the readiness and greatness of the absorption. For a description of the more exact observations made with our absorption-apparatus on both the Nordhausen and ordinary sul-

* Communicated by the Authors.

phuric acid, we would refer to the forthcoming part of the memoir in the 'American Journal of Science.'

1. One cubic inch of pure sulphuric acid, spec. grav. 1·838, was placed in a test-tube, and a stream of dry CO^2 gas, from a self-regulating reservoir, was passed through it for five minutes. On heating the liquid by plunging the tube into boiling water, a slight evolution of gas took place. But when the temperature was raised still higher by a lamp, the gas escaped with a brisk effervescence, and continued to be copiously evolved for several minutes, forming a foamy layer at the top of the liquid. This simple experiment proves clearly enough that a large volume of the gas is absorbed by bubbling through the acid, and points to what takes place in the drying flask of the apparatus of Will and Fresenius. It shows also the important fact, that a temperature much *above that of boiling water* is needed for the effectual disengagement of the absorbed gas.

2. 1 cubic inch of the same acid was introduced into a ground stopper bottle, and briskly agitated for a few minutes with the gas. It was then transferred to a graduated tube over mercury, the column of mercury standing 10 inches above the level of the reservoir. This relief of tension caused at first a free escape of CO^2 from the liquid. 1 cubic inch of previously-boiled water was now let up, which by raising the temperature occasioned a still further evolution of gas. When this had ceased, a lamp-flame applied to the upper part of the tube liberated a large additional volume, and the liquid continued to yield bubbles of the gas even after being boiled for several minutes. When cooled to the surrounding temperature (75°), the instrument was transferred to a large deep reservoir of water, and the levels being adjusted, the gas was found to measure about seven-tenths of a cubic inch. Of this all but a very minute bubble was absorbed by agitation with the water.

Lest it should be supposed that in this and the other experiments in which the acid liquid was boiled in contact with the column of mercury some sulphurous acid might have been evolved, we repeatedly performed the same experiment with boiled water and *unchanged* sulphuric acid; and although the liquid was kept for many minutes in active ebullition close to the surface of the mercury, the only gas evolved consisted of a small bubble, which was unabsorbable by water, and did not therefore contain sulphurous acid.

3. Through 1 cubic inch of the acid in a test-tube, a stream of CO^2 gas was passed briskly for ten minutes. The liquid, transferred to a tall graduated tube over mercury, and diluted with boiled water, and heated as in experiment 2, yielded of gas $\frac{62}{100}$ths of a cubic inch, of which all but a minute bubble disappeared by agitation with cold water.

4. 1 cubic inch of the acid was poured into the graduated tube. Carbonic acid gas was then introduced into the upper space from the jet-tube of the reservoir, and the tube was quickly inverted over mercury. When the sulphuric acid, thus in contact with the CO^2, was agitated, the column was seen instantly to rise, and in a few minutes the absorption amounted to five-tenths of a cubic inch. With

further shaking the absorption was increased, but the action was very slow, on account of the imperfect mode of agitation which the apparatus allowed. The experiment was discontinued when the absorption amounted to about seven-tenths of a cubic inch.

5. 1 cubic inch of the same acid was introduced into a Liebig's apparatus, which was then carefully counterpoised. Carbonic acid, thoroughly dried by being transmitted through a long column of common sulphuric acid, was then made to bubble through the tube for fifteen minutes. The gain of weight was 0·36 gr., equal to $\frac{76}{100}$ths of a cubic inch. The liquid, thus partially charged with carbonic acid, was transferred to the graduated tube, and treated as in experiments 2 and 3. The volume of CO^2 evolved was $\frac{73}{100}$ths of a cubic inch, all of which save a minute bubble was found to be absorbed on agitation with cold water. In this case the heat was not continued long enough to disengage the whole of the absorbed gas. Indeed we have found that even after prolonged boiling the liquid retains a minute portion of the gas.

Similar phænomena present themselves when Nordhausen acid is used instead of acid of the ordinary density, but the absorption is more speedy and of greater extent. It will be seen from the experiments detailed in our memoir, that with Nordhausen acid of spec. grav. 1·87 we found the absorption to be very uniformly about 125 of gas for 100 of the liquid.

The following experiments with the apparatus of Will and Fresenius, used in precise conformity with their directions, will indicate the amount of error which may arise in this process from the retention of CO^2 by the liquids in the two flasks.

1. 70 grs. not very dry carbonate of soda, dissolved in $\frac{3}{4}$ liquid ounce of water, were placed in one flask: in the other was 1 liquid ounce of SO^3. When the reaction was complete, there remained in the latter vessel $\frac{1}{2}$ oz. of SO^3. The aspiration having been continued for some time after the sweet taste ceased to be perceived, the liquids of the two flasks were treated as in the preceding experiments 2, 3 and 5, by heating and dilution over mercury, to separate the retained gas. The result was—

From the mixed liquid..... 0·15 inch carbonic acid.
From the sulphuric acid ..... 0·25 ... ...

making in all 0·40 cubic inches = 0·188 gr.

This corresponds to 0·46 gr. of carbonate of soda, which in 70 grs. amounts to 0·65 per cent. of loss.

2. 60 grs. of thoroughly calcined carbonate of soda were treated with the same quantity of water and acid; the amount of acid suffered to remain unmixed being a little greater than in the preceding case. The aspiration was as before. The result was—

From the mixed liquid ..... 0·27 cubic inch carbonic acid.
From the sulphuric acid .... 0·28 ... ...

making in all 0·55 cubic inch = 0·258 gr.

This corresponds to 0·633 grs. carbonate of soda, or 1·05 per cent.

We would add, that this error may be much reduced by a more

prolonged aspiration; but in this case it is absolutely necessary to annex a drying tube to the opening by which the air enters, to avoid the very considerable gain of weight due to atmospheric moisture. Such an appendage, although not suggested or figured in connexion with the apparatus, would seem, from our trials of the instrument, to be indispensable in all experiments aiming at any degree of accuracy.

On the Existence of Carbonic Acid in Urine and Milk. *By* R. F. Marchand.

Proust long ago stated that urine frequently contained free carbonic acid. There can be little doubt that he separated this acid by boiling the urine, so that it is a matter of uncertainty whether it might not have been formed by the decomposition of the urea. For this reason Berzelius also considered that we ought not to admit the existence of carbonic acid in the urine. A. Vogel however proved that it existed in this fluid, by placing the urine, under the air-pump, in a flask, the conducting tube of which dipped into lime-water, and then exhausting. Bubbles escaped from the urine, and rendered the lime-water turbid. In fresh milk and bile Vogel found doubtful traces of carbonic acid, but he detected large quantities in the blood.

Alexander Marcet had previously performed this experiment with success, whilst Berzelius obtained a negative result; for on covering the urine with olive-oil, which prevented its frothing, he did not find that the lime-water was rendered turbid, and hence drew the conclusion that the turbidness in the former instances merely arose from some of the urine being carried over.

Vogel's statement has therefore not been relied upon, and almost all subsequent writers state that carbonic acid rarely occurs in urine. Lehmann totally denies its existence in healthy urine; Wöhler did not find it in increased quantity after carbonated liquids had been drunk, as Brande stated he had found on several occasions. Marcet did not find Brande's result confirmed, and considered the passage of carbonic acid from the stomach into the urine as very improbable. Marcet however found that carbonic acid was sometimes evolved from urine under the air-pump, at others not; but he was unable to account for this. Wöhler detected carbonic acid in every urine which he examined; he could not determine the quantity, because he merely expelled the whole of the gas contained in the urine by placing it in a Torricellian vacuum. Wöhler adds, that he thinks the urine does not contain more carbonic acid than the blood; and that any increased amount of carbonic acid which enters the body probably passes off through the lungs.

Considering the amount of carbonic acid contained in the blood, the water of which is partly carried off by the kidneys, it would be very remarkable if this were to pass off perfectly free from carbonic acid. As long as the urine does not possess an alkaline reaction, the acid contained in it must exist in a free state. Since the blood

of all animals contains alkaline carbonates, which pass into the urine, in consequence of the acid nature of the latter carbonic acid must necessarily exist in it.

I examined the urine as to this point in the following simple manner:—The fluid, immediately after it had been passed, was placed in a tall bottle, which was half-filled with it. The bottle was closed with a cork, through which two glass tubes were passed. One of these tubes was straight, and dipped a little beneath the surface of the urine, and extended about 4 to 5 inches above the neck of the bottle. The other was bent twice at right angles; this formed the conducting-tube, and dipped into a bottle filled with barytic water*. This was also closed with a cork having two holes in it, through one of which a tube similar to the former passed; another, also bent twice at right angles, passed through the second hole, and extended to the bottom of a second bottle containing barytic water. This bottle, lastly, was closed in the same manner, except that the conducting-tube did not dip into barytic water, but opened into the air.

When the apparatus was placed under the receiver of the air-pump, and this was slowly exhausted, the urine rose in the straight tube of the bottle; at the same time air escaped from the conducting-tube through the barytic solution. If it contained carbonic acid, the almost perfectly-clear liquid became turbid. When the air is admitted into the receiver, the barytic water does not ascend into the urine, because air can enter through the upright tube. I have repeated the experiment in this manner more than twenty times; the urine of persons of the most different constitutions always contained carbonic acid provided that it had an acid reaction.

I have examined the morning urine and the evening urine, immediately after immersion in a cold-water bath for half an hour; it was very aqueous, and had a specific gravity of 1·0045; the evolution of carbonic acid always occurred†.

It appeared to me of interest to determine, at least approximately, the amount of the acid existing in the gaseous state. 330 grms. of urine (12 at noon, milk and bread only having been previously taken on that day), of 1013 spec. grav., were treated in the above manner.

As the urine was still warm when placed under the air-pump, the evolution of gas was very copious, and an inconsiderable amount only of carbonic acid could have remained in the urine. The carbonate of baryta was converted into sulphate of baryta, and its weight determined.

It amounted to 0·214 grm., thus corresponding to 0·0403 grm. or 20 cb. c. of carbonic acid.

* Barytic water is preferable to lime-water; its reaction is decided and instantly evident. Undoubtedly a negative result, in many of the earlier experiments, has been obtained in consequence of the use of lime-water.

† To be certain that none of the urine spirted over, which without this precaution may easily occur, I covered the urine with oil, without at all diminishing the evolution of the carbonic acid.

Shortly after the noon meal, which consisted of soup, roast meat and vegetables, 495 grms. of urine, of 1014 spec. grav., gave 0·359 grm. of sulphate of baryta, or 0·0677 grm. of carbonic acid, corresponding to 34·1 cb. c.

The urine of an infant, eighteen months old, also gave a distinct evolution of carbonic acid.

The carbonic acid may be completely expelled from the liquid and determined quantitatively, by placing the urine in a glass flask, which is closed by a cork perforated with two holes. Through one hole an upright tube passes air-tight; this dips into the urine, and terminates at the other end in a fine and easily-fused point. Through the second hole a doubly-bent tube passes; this extends into an empty bottle, through a cork which closes it air-tight; from this, through the same cork, a second tube passes, which extends into a bottle arranged in a similar manner, and filled with barytic water, to which a second and third bottle containing barytic water are adapted. The latter is connected with the air-pump. If the apparatus is found to be perfectly air-tight, the urine is heated in a water-bath to 120°–140° F., and the pump then slowly set in motion. The liquid soon begins to boil most violently, and to distil into the empty flask as the receiver; the barytic solutions become turbid; when the ebullition has lasted from a half to three-quarters of an hour, the point of the first upright tube is broken off, and air is drawn several times through the apparatus, more than is sufficient to free it from the carbonic acid. The carbonate of baryta is weighed, or as above converted into sulphate of baryta, and the amount of carbonic acid calculated from its weight.

326 grms. of urine, of 1·012 spec. grav., yielded 0·286 grm. of sulphate of baryta, or 32 cb. c. of carbonic acid.

225 grms. of urine, of 1·017 spec. grav., yielded 0·205 grms. of sulphate of baryta, or 23 cb. c. of carbonic acid.

On examining the urine after a large quantity of artificial Seltzer water had been drunk, the evolution of carbonic acid was by no means great. It amounted in two experiments, in 200 cb. c. of urine, to 21 cb. c., and in 255 cb. c. to 26 cb. c. of carbonic acid.

This result agrees with that obtained by Wöhler.

Carbonic acid is not the only gas contained in urine. We may easily satisfy ourselves that the elements of atmospheric air exist in it. Their quantity is extremely small, so that the exact determination of it is very difficult. In the fresh fluid of ascites I was unable to detect carbonic acid, although it contained abundance of urea.

But carbonic acid always exists in fresh milk. This fluid was drawn directly from the cow into the vessel in which the experiment was performed. Under the air-pump there was a slight but still decided evolution of carbonic acid, which increased when it was heated to boiling. The milk had an alkaline reaction, so that the carbonic acid existed in it either in the form of a bicarbonate, or as absorbed by an alkaline phosphate.

Fresh ox-bile gave slight but distinct indications of the presence of carbonic acid.—*Journ. für Prakt. Chem.*, No. xii. 1848.

On the Essential Oils. *By* C. GERHARDT.

In the following experiments the author shows that the essential oil of chamomile is a mixture of a hydrocarbon, $C^{20}H^{16}$, belonging to the camphene class, and of an oxygenated oil, $C^{10}H^{8}O^{2}$, which constitutes the aldehyde of angelicic acid, and is converted into the latter by fusion with potash, and into valerianic acid, $C^{10}H^{10}O^{4}$, by the action of an alcoholic solution of potash. The essential oil of rue is composed, for the greater part, of an oxygenated oil, $C^{20}H^{20}O^{2}$, which behaves like the aldehyde of capric acid; and is converted by nitric acid, either directly into capric acid, $C^{20}H^{20}O^{4}$, or into homologous acids containing less carbon, amongst which pelargonic acid, $C^{18}H^{18}O^{4}$, is most abundant.

Oil of Anthemis nobilis.—Chamomile oil is of a greenish colour, has an agreeable odour, and begins to boil at 320°; however, the boiling-point gradually rises to 374°, at which point it remains for a long time stationary. More than two-thirds of the oil pass over at this temperature. The temperature then rises to 410°; however, no distinct oil possessing this boiling-point is found in the residue; but the rise is entirely owing to the presence of a resinous substance, for the first and last portions of the distillate exhibit the same reactions, and are consequently composed of the same principles. These principles have their boiling-points so near together, that they cannot be separated by distillation. Three portions of the oil, collected between 392° and 410°, afforded the following results:—

Carbon	75·57	76·61	76·00
Hydrogen	10·57	10·66	10·78
Oxygen	13·86	12·73	13·22

This composition would seem to express that of a simple body; but it was subsequently found that the oil analysed had a strong acid reaction, and, like the first portions, gave with potash a certain quantity of carburetted hydrogen.

As is well known, potash is often employed advantageously to separate oxygenated oils from the hydrocarbons which accompany them; it was by this means the author prepared the hydrocarbons of the oils of cumin and valerian. The oxygenated principles are converted into acids, which combine with the potash, and the hydrocarbon then distils over pure. An aqueous solution of potash does not act on oil of chamomile; when it is gently heated with pulverized hydrate of potash, the whole concretes to a gelatinous mass without any disengagement of gas, and the oil is separated unaltered by water; but if the gelatinous product is heated further, or if chamomile oil is heated with an alcoholic solution of potash, the oxygenated principle is converted into an acid, and the hydrocarbon is set free. The acids which are formed under these circumstances are the angelicic and valerianic acids.

Angelicic Acid.—When the oil is fused with an excess of potash, the mass puffs up considerably, owing to the disengagement of hydrogen; at the same time a liquid having the agreeable odour of lemons, condenses, which consists of a hydrocarbon, to which we

shall presently return. On saturating the potash residue with sulphuric acid, acrid vapours similar to those of benzoic acid are given off, which condense readily into beautiful needles. They crystallize readily from water, and are very fusible; they melt in hot water, and the solution gives off on boiling acrid vapours. On analysis they yielded—

Carbon	59·7	10	60·0
Hydrogen	8·0	8	8·0
Oxygen	32·3	4	32·0

numbers which represent the composition of the acid extracted by Meyer and Zenner from the root of Angelica. This acid is the cause of the acidity of the oil of chamomile, and appears to be formed by the further oxidation of the oxygenated principle.

Valerianic Acid.—When oil of chamomile is boiled for some minutes with an alcoholic solution of potash, the whole of the oxygenated portion combines with the potash, and the alcohol only contains in solution the hydrocarbon previously mentioned. This and the alcohol are removed by distillation, and the dry residue decomposed by sulphuric acid, which separates an oily acid possessing the odour and the properties of valerianic acid. As thus obtained, it is frequently contaminated by a certain quantity of angelicic acid, which is removed by rectifying the oily acid separated from the potash salt, taking care to allow the liquid scarcely to boil; the angelicic acid then remains in the residue, and separates on cooling in beautiful needles.

Hydrocarbon.—We have seen above that on treating the oil of chamomile with solid potash or an alcoholic solution of potash an oil is set free upon which this agent has no action. To obtain this oil perfectly dry, it must be rectified over potassium, for the chloride of calcium dissolves a small portion producing a crystalline compound which is decomposed by water. If an alcoholic solution of potash has been employed to saponify the oil of chamomile, water is added to the mixture so as to separate the oil, and the liquid is then saturated with chloride of calcium, and the oil removed with the pipette.

When perfectly pure, this oil has a very agreeable odour of lemons, like cymene; its boiling-point is likewise 347°; but there is no identity between the two oils, as the following analysis will show:—

Carbon	87·8
Hydrogen	11·8

Moreover, it does not furnish any conjugated compound with sulphuric acid, as is the case with cymene.

Composition of the Oxygenated Principle.—It is impossible, as above stated, to extract the principle which furnishes, under the influence of potash, the angelicic and valerianic acid in a state of purity; even when only the last portions of the distillate are collected, they always contain some hydrocarbon; however, the reactions with potash indicate in a positive manner the composition of the oxygenated principle.

Angelicic acid and valerianic acid contain the same amount of carbon, C^{10}; the first acid contains 2 equivs. of hydrogen less than the other. Now in the formation of the valerianate of potash there is no disengagement of gas, whilst the formation of the angelicate is accompanied by a liberation of hydrogen; consequently the oxygenated principle of the oil of chamomile must contain $C^{10} H^8 O^2$, since—

Valerianate of potash, $C^{10} H^8 O^2 + KO + HO = C^{10} H^9 O^3 + KO$.
Angelicate of potash, $C^{10} H^8 O^2 + KO + HO = C^{10} H^7 O^3 + KO + H^2$.

The author has moreover ascertained that the valerianate is not converted *per se* into angelicate. Some pure valerianate of potash was fused with an excess of potash at 572° and somewhat above, which temperature is much higher than that at which the angelicate is formed from the oil, and there was no disengagement of gas. Besides, the presence of free angelicic acid in the oil is in favour of the preceding formula for angelicic acid $= C^{10} H^8 O^2 + O^2$.

The following fact is equally conclusive: the hydrocarbon of the oil being $C^{20} H^{16}$ or $C^{10} H^8$, and the free acid occurring in it likewise containing $C^{10} H^8$, it is evident that we ought always to find in the crude oil of chamomile this relation of $C^{10} H^8$, whatever proportions of acid hydrocarbon and oxygenated oil it may contain, that is to say, at whatever period it is collected in the distillation. Take, for instance, the three analyses above-mentioned, and we find—

Carbon..... 76·1 : 6 = 12·68 equivs. carbon.
Hydrogen ..... 10·6 : 1 = 10·6 equivs. hydrogen,

or 12·68 : 10·6, very nearly as 10 : 8.

The author once obtained, in the rectification of an oil of chamomile which contained a little alcohol, a perfectly blue distillate, which colour disappeared in the course of eight days. Whether the blue oil of *Matricaria chamomilla* contain the same constituents as the oil of *Anthemis nobilis* is unknown; but it is remarkable that the analyses by Bornträger of the oil of the common chamomile give the relation $C^{10} : H^8$.

Oil of Rue.—The essential oil of rue, *Ruta graveolens*, analysed a few years ago by Dr. Will, is regarded by that chemist as the oxide of a hydrocarbon, $C^{28} H^{28} O^3$, which formula corresponded, according to him, to 4 vols. vapour. As this composition is opposed to the views entertained by MM. Laurent and Gerhardt respecting the formulæ of organic compounds, the author has made some experiments on the subject.

The oil of rue begins to boil at 424°, but gradually it rises to 438°, where it remains nearly stationary. When rectified, it boiled at 451°. The following is the analysis of the first portions of the distillate:—

Carbon.....	77·65
Hydrogen	12·80
Oxygen	9·55

These numbers evidently represent the composition of a mixture

On the other hand, if the last third of the distillate is collected, a perfectly distinct substance is obtained, as the following analyses prove:—

Carbon	76·69	76·95	20	76·92
Hydrogen	12·87	12·85	20	12·84
Oxygen	10·44	10·20	2	10·24

The oxygenated principle of the oil of rue is consequently isomeric with the solid portion of the essential oil of mint; moreover, Cahours has shown that the oil of rue may be rendered solid by cold; and the crystals furnished him on analysis results identical with the above and the density of the vapour 5·83, which shows that the formula $C^{20}H^{20}O^{2}$ corresponds to 2 vols.

When oil of rue is mixed with potash-lime, it enters into combination with it; and on heating the mixture beyond the boiling-point of the oil, to 554° for instance, no disengagement of gas is perceptible. The residue is yellowish, and when dissolved in hydrochloric acid furnishes a residue mixed with a large quantity of unaltered oil. When the oil of rue is passed over chloride of zinc in a state of fusion, it is decomposed, and furnishes a hydrocarbon, the composition of which was not ascertained.

A compound isomeric, or perhaps polymeric, with the oil of rue, was obtained by dissolving the oxygenated constituent in from 3 to 4 times its volume of spirit, and passing into the solution muriatic acid gas. When the mixture fumed and had acquired a brown colour, the more volatile portions were expelled, and the residue mixed with water. The oil which separated had a very agreeable fruity odour, very different from the disagreeable odour of the oil of rue. It boiled however at the same temperature, between 446° and 455°; it was not acted upon by potash. After some time it solidified at a temperature at which the oil of rue remains perfectly liquid; the crystals melted at 55°, and gave on analysis—

Carbon.....	77·10
Hydrogen	12·95
Oxygen	9·95

or pretty nearly the same numbers as those obtained in the analysis of the oil itself. These crystals dissolve readily in cold concentrated sulphuric acid, scarcely imparting any colour to it; if the mixture is heated, a conjugated acid is produced, the baryta salt of which is soluble in water. The oil of rue yields nothing similar.

The composition of the oil of rue corresponds to that of the capric aldehyde; it presents with nitrate of silver the reaction peculiar to the aldehydes; an aqueous solution of nitrate of silver has scarcely any action upon it; it separates on boiling, but the ammoniacal nitrate of silver is quickly reduced; at this temperature the oil becomes covered with a mirror-like pellicle, and the sides of the vessel in contact with it present the same appearance. This reduction of the nitrate of silver led the author to think that other oxidizing agents would furnish capric acid, or at least a homologue. However, the

isomeric body above-mentioned does not exhibit this phænomenon of reduction.

Action of Nitric Acid: Production of Capric and Pelargonic Acids.—Boiling nitric acid quickly oxidizes the oil of rue; the product most readily obtained under these circumstances is an oily acid, which has all the properties of the pelargonic acid discovered by Pless in the leaves of *Pelargonium roseum*, and obtained by Redtenbacher by acting upon oleic acid with nitric acid. However, by using a less concentrated acid and moderating the reaction, a more highly carbonized acid, the capric acid, is obtained instead of pelargonic acid. Cahours states that he has obtained an acid, $C^{20}H^{20}O^4$, which he calls rutic acid, but which is undoubtedly the capric acid.

1 part of the essential oil was heated gently with 1 part of ordinary nitric acid diluted with its volume of water. At first the reaction was very lively, and it became necessary to remove the mixture from the fire; the reaction nevertheless still proceeded; it was subsequently boiled, returning the distillate until no more red vapour appeared. It was decanted, washed with water, and treated with caustic potash, which separated a quantity of a non-acid oil of a very acrid odour. The potash solution was then decomposed with sulphuric acid, which liberated an oily acid contaminated with a resinous substance, which coloured all the salts and prevented them from crystallizing; it was consequently necessary to purify the acid by distillation. The rectified acid was mixed with caustic baryta, washed with cold water to remove the excess of baryta, and boiled with alcohol; the filtered solution then solidified into a mass of white nacreous laminæ. Several successive crystallizations furnished the same salt, which yielded 30·2, 30·4, 30·2 per cent. barium; the formula for the pelargonate of baryta, $C^{18}H^{17}O^3$, BaO, requires 30·2 per cent. barium.

The preceding salt was dissolved in boiling water and filtered, for the greater part of the salt does not dissolve. After having added some more water, the solution was boiled, and some nitrate of silver poured into it; this furnished a very bulky white precipitate, which, washed with boiling water and dried at 320°, gave on analysis—

Carbon	40·3	18 =	108	40·7
Hydrogen	6·4	17	17	6·4
Oxygen	12·4	4	32	12·2
Silver	40·8	1	108	40·7

A quantity of the pelargonate of baryta was decomposed with dilute sulphuric acid; the pelargonic acid came to the surface in the form of a colourless oil, of a faint odour like that of butyric acid. During the night it solidified (it was in the month of January, and had been very cold), and again became liquid the next morning, when the temperature of the laboratory was at 50°. Pelargonic acid is almost insoluble in water; it distils without alteration at a high temperature.

When mixed with ammonia and heated gently, pelargonic acid

furnishes a transparent gelatinous mass; by the addition of a large quantity of hot water the salt redissolves, giving a milky solution like soap-water. On cooling it solidifies to a paste, which is very soluble in cold alcohol. An alcoholic solution of this pelargonate of ammonia, mixed with an aqueous solution of nitrate of copper, furnished an abundant greenish-blue precipitate, soluble in boiling alcohol. On evaporating the alcoholic solution, after expelling the greater part of the alcohol, some green oily drops make their appearance, which solidify on cooling. Boiled with alcohol, this product deposits on cooling bluish-green crystalline granules of the pelargonate of copper, $C^{18} H^{17} O^3, CuO + 2aq$, which requires 19·2 per cent. copper; analysis gave 19·3 per cent.

The preceding experiments place beyond all doubt the formation of pelargonic acid by the oxidation of the oil of rue; however, as this contains C^{20}, it is evident that it is not the immediate product of the oxidation. In two experiments a salt of baryta was obtained, which was far less soluble in alcohol than the pelargonate, and corresponded exactly in composition to the caprate of baryta, which requires 28·4 barium, while analysis gave 28·2.

The oily acid separated from the salt by sulphuric acid possesses the peculiar odour of capric acid. M. Cahours' experiments have led to the same result; however, the oxidation of the oil of rue by nitric acid does not always stop at a mere fixation of oxygen; in one operation a baryta salt, still far more soluble than the pelargonate, was procured, which evidently corresponded to some less carbonated homologue.—*Ann. de Chim. et de Phys.*, Sept. 1848.

On some Phosphates of the Protoxide of Manganese.
By W. Heintz.

Phosphate of the Protoxide of Manganese, $MnO, 2HO + PO^5 + 2HO$, is formed when the precipitate, which the ordinary phosphate of soda produces in a solution of a protosalt of manganese, is dissolved in phosphoric acid, and this liquid evaporated (I. II.); or when an excess of recently-precipitated $3MnO + PO^5$ is boiled with phosphoric acid, evaporated to a syrupy consistence, and set aside to crystallize (III. IV.). In either way, groups of minute prismatic crystals are obtained, which dissolve easily in water. Alcohol, especially boiling, does not dissolve the dry salt, but removes phosphoric acid from it, and converts it into the salt containing 1 atom acid to 2 of protoxide of manganese. The aqueous solution is precipitated by alcohol, but it is no longer the same salt, phosphoric acid being removed by the alcohol.

It melts easily before the blowpipe upon charcoal in the oxidizing flame, with the escape of phosphoric acid and phosphorous in luminous bubbles, to a black bead, which, when spread out into a thin plate, is transparent and violet. In the reduction-flame the bead becomes instantly white and opake; this bead reacquires the black colour in the oxidizing flame. When heated to between 230° to 248°, it loses

2 atoms of water of crystallization, and on ignition, 2 atoms of basic water. The salt contains in 100 parts—

	I.	II.	III.	IV.		
Water (of crystallization)	13·19	13·24	13·38	12·60	2	12·60
Water (basic)	13·24	12·77	13·04	12·60	2	12·60
Protoxide of manganese	25·32	24·60	24·88	24·88	1	24·88
Phosphoric acid.....	48·98	49·17	49·37	49·92	1	49·92

Diphosphate of the Protoxide of Manganese, $(2MnO + HO) + PO^5 + 6HO$, is formed when the solution of the protosulphate of manganese is acidulated with acetic acid, more slowly when muriatic or phosphoric acid is used, and c-phosphate of soda added until the precipitate remains permanent. The whole of the manganese must not be thrown down. The precipitate becomes crystalline after some time; the crystals are white and granular; the larger ones have a reddish tint. This salt is also left as an insoluble residue, which after some time becomes crystalline, when an excess of $3MnO + PO^5$ is boiled with phosphoric acid, and the solution of $MnO, 2HO + PO^5$ produced is removed. The crystals dissolve with difficulty in acetic acid, readily in strong mineral acids, with difficulty in water, and not in alcohol. This salt does not fuse so readily before the blowpipe as the preceding and following salts, but exhibits on the whole the same reactions. The analyses show that 5 atoms of water of crystallization are expelled between 212°–248°, another atom at 392°, and 1 atom of basic water on ignition; so that the formula of this salt should probably be $2MnO, HO + PO^5 + HO + 5HO$. It furnished—

Water (at 212°).....	22·02	22·09	23·30	5	21·90
Water (at 392°).....	4·23	8·97	7·87	1	4·38
Water (basic).....	4·57			1	4·38
Protoxide of manganese....	..	34·43	34·58	2	34·61
Phosphoric acid.....	..	34·86	34·61	1	34·73

Trisphosphate of the Protoxide of Manganese, $3MnO + PO^5 + 7HO$, falls as a white powder, sparingly soluble in water, when a solution of protosulphate of manganese is precipitated with an excess of c-phosphate of soda. It forms a loose powder, which is not crystalline under the microscope, is insoluble in alcohol, tolerably soluble in acetic acid, and easily soluble in strong acids. It resembles the two preceding compounds in its behaviour before the blowpipe.

This salt has been regarded by Berzelius as $2MnO + PO^5$; it possesses the properties described by him. On treatment with ammonia, it passes into the double salt described by Otto, $NH^4O, 2MnO + PO^5 + 2HO$, and loses between 230° and 248° 4 atoms, and on ignition 3 more atoms of water. The formula is probably $3MnO + PO^5 + 3HO + 4HO$. The analysis gave—

Water (at 248°).....	15·95	15·85	..	4	14·94
Water (on ignition)	11·15	11·10	11·39	3	11·20
Manganese.....	43·66	..	43·91	3	44·26
Phosphoric acid.....	29·82	..	29·32	1	29·90

Diphosphate of the Protoxide of Manganese and Ammonia, NH^4O, $2MnO + PO^5 + 2HO$, was obtained by the process described by Otto, but without the application of heat, by dropping c-phosphate of soda into a faintly-ammoniacal solution of protosulphate of manganese. Between 230° and 248° it lost merely hygroscopic water. The analysis made by Otto is added for comparison:—

	Heintz.	Otto.
$NH^4O + 2HO$	24·51	23·30
$2MnO$	38·35	37·84
PO^5.....	38·37	37·86

When the solution of the sulphate of the protoxide of manganese is imperfectly precipitated with c-phosphate of soda, it acquires an acid reaction, and the precipitate consists, at least in part, of a trisphosphate—Poggendorff's *Annalen*, lxiv. p. 449.

On the Action of Cyanogen upon Iodoform. By E. St. Evre.

When a current of cyanogen is passed in excess into an alcoholic solution of iodoform, the liquid becomes heated, and assumes a violet tint, which gradually grows darker and darker. When set aside it soon deposits prismatic crystals of a golden colour. By means of cold weak alcohol it may be separated into two distinct substances, both possessing a metallic lustre in the highest degree, the one violet, the other a golden green. The first exhibited on analysis the composition of cyanogenated iodoform, and corresponds to the formula $C^4H^2I^4, C^4N^2 = C^8H^2I^4N^2$; it contains in round numbers 87 per cent. iodine, whilst iodoform contains 97. The second substance contains still less iodine.—*Comptes Rendus*, Nov. 20, 1848.

On the Precipitation of Iron from Solutions of the Alkaline Tartrates by Alkaline Hydrosulphurets. By H. Blumenau.

Wishing to purify a solution of tartrate of potash, which contained much carbonate of potash, from a considerable amount of iron, I mixed it with a large quantity of hydrosulphuret of potassium. The liquid became yellow, but to my astonishment deposited mere traces of the sulphuret of iron. A further addition of the sulphuret of potassium produced but little change, and it required a considerable excess to precipitate the whole of the iron. The sample now contained an extraordinary amount of hydrosulphuret of potassium, along with carbonate and tartrate of potash. This difficult precipitation was so remarkable, that it induced me to make some experiments on the subject; these led to the result, that the iron is only precipitated readily and entirely by hydrosulphurets from solutions of the fixed alkaline tartrates, which contain a large excess of carbonated alkali when the latter is previously neutralized, and the solution is kept as close as possible to the point of neutralization, or is even *very* faintly acid. No excess of the alkaline sulphuret is then required, and both the atoms of sulphuretted hydrogen contained in it are available, 1 atom of which it is true is only set free by the reaction to become again instantly decomposed.

When a very alkaline solution of tartrate of potash containing iron is mixed with a little hydrosulphuret of potassium or ammonium, the liquid becomes yellow or green, as above stated, and deposits mere traces of a precipitate even when kept for several days; now when a solution of tartaric or any other acid is dropped into this yellow clear solution, the liquid becomes thick and black immediately; and if perfectly neutral, the whole of the iron is separated, and the liquid becomes transparent. If only a few drops of an acid be added to it, so that it has a faint acid action upon blue litmus-paper, the sulphuret of iron is quickly deposited, without in the least being affected by the small excess of acid.—Liebig's *Annalen*, July, p. 125.

PATENT.

Patent granted to Alexander Parkes, Birmingham, *for Improvements in the Manufacture of Metals, and in coating Metals.*

The first part of this invention, which relates to the improvements in the manufacture of metals, consists in separating copper and some other metals from their sulphuretted ores into the state of regulus or coarse metal; also in obtaining the metal by one process or operation of melting from a regulus or other sulphuret of a metal.

In order to obtain a regulus of copper from a sulphuret, the patentee takes the usual precautions adopted by smelters to form a fusible slag; that is to say, by a due admixture of the ores themselves, or of the ore with other matters, as fluxes. To every ton of such ores, when containing about 10 per cent. of metal, he adds, either before or whilst the same are in the melted state, from 100 to 150 lbs. of sulphate of lime, or of soda, or of baryta, or of potash; he keeps the whole in a melted state until the regulus becomes separated from the earthy matters; and then he taps the furnace into sand or water; sometimes, when operating in this way, he adds a carbonate or oxide ore, whereby he obtains a regulus more rich in metal. The regulus or product thus obtained may be treated in the usual way to obtain the metal therefrom, or it may be treated in the manner hereafter described. The sulphuret ores of silver and antimony may be treated in the same way as the sulphuret ores of copper; but when the sulphuret ores of silver are to be operated upon, from 5 to 10 per cent. of scrap iron should be added. Although only the sulphates of lime, soda, baryta and potash are mentioned in the above description, yet the sulphurets of the same substances, and other sulphates and sulphurets, may be employed.

The mode of treating the regulus obtained as above described, or other regulus or sulphuret of copper, in order to obtain the metal by one operation of melting, is as follows:—The principle on which the patentee acts is, to mix with a regulus or other sulphuret of copper such a metallic compound, that the oxygen which it contains shall desulphurize the sulphuret in the act of melting, and allow the metal to separate. For this purpose the patentee employs a carbo-

nate or oxide of copper, and thereby obtains copper fit for refining by the ordinary process; or he uses a carbonate or oxide of zinc, in which case a great part of the zinc will form an alloy with the copper. When zinc is employed, it will be requisite to use the flux hereafter described. The sulphates of copper, iron and zinc will also answer; but they will require to be used in larger proportions than the oxides, and are not so advantageous. When reducing a regulus or sulphuret of copper, containing about 30 per cent. of copper, the patentee prefers to use a carbonate or oxide of copper containing the same per-centage of metal, and he takes equal quantities by weight of the two matters; but if the sulphuret contains more sulphur than is equivalent to the oxygen contained in the oxide, he adds a larger proportion of the oxide compound. He first fuses the sulphuret, removing any slag that forms previous to introducing the oxide or carbonate, which he does by degrees, occasionally removing the slag, and gradually adds about 10 per cent. of a flux, composed of carbonaceous matter and chloride of calcium or chloride of barium, in equal proportions. In from three to six hours the sulphuret will be decomposed and the metal separated.

The above process is also applicable to the sulphurets of silver and antimony. When operating upon the sulphuret ores of silver, the patentee prefers to obtain the regulus by the method above described for treating copper ores; and he subsequently decomposes the same by the carbonate of zinc or of copper, using therewith from 5 to 10 per cent. of scrap iron. When a sulphuret of antimony is to be treated, if it contain much earthy impurity it is fused in the manner described when obtaining a regulus of copper, and the product is calcined at a low temperature; the oxide thus obtained is fused with an equal quantity of sulphuret of antimony, which has not been calcined (a flux being added, as directed for copper); and thereby the metal is separated.

Sometimes, instead of using oxidized compounds of metal as the means of decomposing sulphurets of copper at one operation of melting, the patentee employs the oxygen of the air. He acts on melted regulus of copper (which should contain at least 30 per cent. of copper) in a reverberatory furnace, by causing currents of air, either hot or cold, to be forced in contact with the melted materials (suitable openings being made for this purpose in the fire-bridge, or in the roof or other part of the furnace); the slag is removed from time to time as it forms; and the sulphuret becomes progressively decomposed and the metal separated.

The improvements in coating metals relate to iron and steel, and consist in the use of an alloy composed of about 9 parts of lead and 3 parts of antimony, or about 9 parts of lead, 1 part of tin and 1 part of antimony; these metals are fused and kept in a melted state beneath a flux of considerable depth, composed of chloride of barium or chloride of sodium, or a mixture of these two materials; and the articles to be coated, having been first carefully cleaned, are immersed in the melted metal until the desired coating is obtained.—Sealed April 27, 1848.

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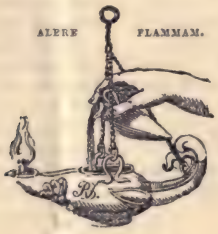

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